

PB83-263251

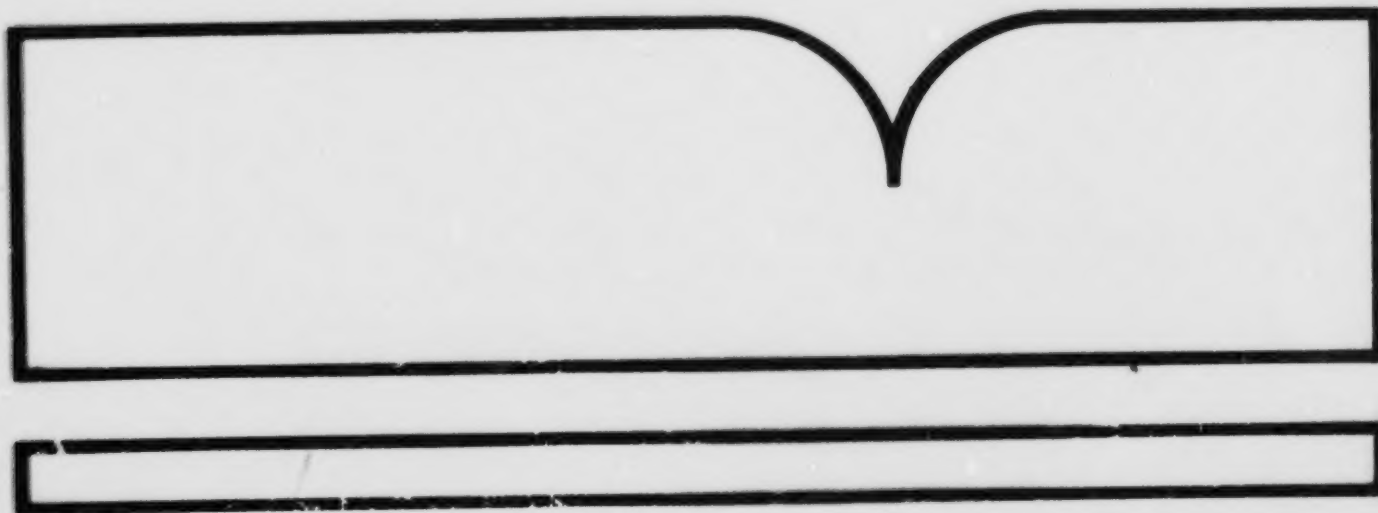
Evaluation of Chemical Reaction
Mechanisms for Photochemical Smog. Part 1
Mechanism Descriptions and Documentation

California Inst. of Tech., Pasadena

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

Sep 83



U.S. Department of Commerce
National Technical Information Service

NTIS

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
1. REPORT NO. EPA-600/3-83-086	2.	3. RECIPIENT'S ACCESSION NO. PB83 263251
4. TITLE AND SUBTITLE EVALUATION OF CHEMICAL REACTION MECHANISMS FOR PHOTOCHEMICAL SMOG. PART I. MECHANISM DESCRIPTIONS AND DOCUMENTATION	5. REPORT DATE September 1983	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) G. J. McRae, J. A. Leone, and J. H. Seinfeld	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS California Institute of Technology Pasadena, CA 91125	10. PROGRAM ELEMENT NO. CDWALA/01-2048 (FY-83)	
	11. CONTRACT/GRANT NO. Cooperative Agreement 810184	
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory-RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED Interim (7/82-4/83)	
	14. SPONSORING AGENCY CODE EPA/600/09	
15. SUPPLEMENTARY NOTES		
16. ABSTRACT Documentation on six chemical kinetics mechanisms that have been developed to describe photochemical smog formation is provided. The six mechanisms are (1) the Carbon Bond Mechanism III developed by Systems Applications, Inc., (2) the surrogate species mechanism developed by Atkinson, Lloyd and Wings, (3) the LIRAQ mechanism developed by Penner and Walton, (4) the generalized species mechanism developed by McRae and Seinfeld, (5) EPA's Photochemical Box Model mechanism and (6) the chemical mechanism currently used in the Empirical Kinetics Modeling Approach (EKMA). This volume (Part I) contains a description of the mechanisms, including an analysis of the treatment of the basic chemistry, how to specify photolysis rate constants and how to determine initial conditions and reaction rate constants for lumped organic species. Part II is devoted to a detailed analysis of the behavior of each mechanism.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 172
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA-600/3-83-086
September 1983

EVALUATION OF
CHEMICAL REACTION MECHANISMS FOR PHOTOCHEMICAL SMOG
PART I. MECHANISM DESCRIPTIONS AND DOCUMENTATION

by

Gregory J. McRae
Joseph A. Leone
John H. Seinfeld

California Institute of Technology
Pasadena, California 91125

Cooperative Agreement 810184

Project Officer

Marcia C. Dodge

Gas Kinetics and Photochemistry Branch
Environmental Sciences Research Laboratories
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

Over the past ten years or so a great deal of effort has been devoted to developing chemical reaction mechanisms for photochemical air pollution. Because the actual number of atmospheric organic species is too large for the detailed chemistry of each to be included in a mechanism, it has been necessary to reduce the number of organic species to a manageable set by a process referred to as lumping. The manner in which this lumping has been carried out constitutes one of the major differences among existing mechanisms. It has recently been demonstrated that different chemical mechanisms predict different degrees of hydrocarbon and NO_x control to achieve the same level of ozone reduction under identical conditions. Because of the necessity of using reaction mechanisms for photochemical smog in determining air pollution control strategies, these results point to a serious need to analyze the fundamental behavior of such mechanisms and to understand the key elements of their behavior. Such an analysis is the subject of this two part report. The current volume, Part I, contains a detailed description of six mechanisms that have been developed to describe photochemical smog chemistry, including analyses of the treatments of the basic chemistry, of photolysis reactions and organic lumping in initial conditions and rate constants. It is found that the mechanisms differ in virtually all aspects. Part II is devoted to a detailed analysis of the behavior of each of the mechanisms.

TABLE OF CONTENTS

ABSTRACT	iii
LIST OF FIGURES	vii
LIST OF TABLES	viii
ACKNOWLEDGEMENT	
CHAPTER 1 INTRODUCTION	1
CHAPTER 2 DOCUMENTATION AND INITIAL TESTING OF REACTION MECHANISMS	10
2.1 The Reaction Mechanisms	10
2.2 Numerical Solution of the Chemical Kinetics	40
2.3 Implementation and Initial Mechanism Testing	41
CHAPTER 3 DISCUSSION OF THE CHEMICAL FORMULATION OF THE MECHANISMS	43
3.1 Carbonyl Chemistry and Lumping	43
3.2 Alkane Photooxidation Chemistry	55
3.2.1 Generalized Species Lumped Molecule Mechanisms	62
3.2.2 Carbon Bond Mechanism (KW)	62
3.3 Alkene Photooxidation Chemistry	64
3.3.1 Alkene-O and Alkene-OH Reactions	64
3.3.2 Alkene-O ₃ Reactions	71
3.4 Aromatic Photooxidation Chemistry	79
3.4.1 Toluene-OH Reaction	79
3.4.2 x-Xylene-OH Reaction	79
3.4.3 Treatment of Aromatic Photooxidation by the ALW Mechanism	79
3.4.4 Treatment of Aromatic Photooxidation by the KW Mechanism	87
3.4.5 Evaluation of the Aromatic Hydrocarbon Reactions in the Generalized Species Mechanisms	90

CHAPTER 4	SPECIFICATION OF PHOTOLYSIS RATE CONSTANTS	93
4.1	Methods for the Determination of Photolysis Rate Constants	93
4.2	Specification of the Actinic Irradiance	98
4.3	Scaling of Photolysis Rates in Atmospheric Applications	99
4.4	Specification of Mechanism Photolysis Rate Constants	103
4.5	Uncertainty Estimates for the Photolysis Rates	115
CHAPTER 5	SPECIFICATION OF INITIAL CONDITIONS AND REACTION RATE CONSTANTS FOR LUMPED ORGANIC REACTIONS	120
5.1	Species Assignment to Lumped Hydrocarbon Classes	120
5.2	Calculation of Lumped Reaction Rate Constants	134
5.3	Atmospheric Modeling Applications	138
5.4	Conclusions	149
CHAPTER 6	CONCLUSIONS	151
REFERENCES		153

LIST OF FIGURES

1	Classification of Photochemical Reaction Mechanisms Used in Evaluation	3
2	Formaldehyde, Acetaldehyde and Propionaldehyde Photooxidation Mechanisms	46
3	Acetone and Methyl Ethyl Ketone Photooxidation Mechanisms	47
4	n-Butane Photooxidation Mechanism	58
5	2,3-Dimethyl Butane Photooxidation Mechanism	59
6	Ethene, Propene, Trans-2-Butene-O Reaction Mechanism	67
7	Ethene, Propene, and Trans-2-Butene-OH Reaction Mechanism	68
8	Toluene-OH Abstraction Pathway Reaction Mechanism	80
9	Proposed Toluene-OH Addition Pathway Reaction Mechanism	81
10	m-Xylene-OH Addition Pathway Reaction Mechanism	82
11	Classification of (a) Propylene and (b) Cis-2-Butene into the Carbon-Bond Categories	133

LIST OF TABLES

1	Photochemical Reaction Mechanisms Considered for Evaluation Their Characteristics and Their Validation Base	7
2	Definition of the Atkinson et al. (1982) Reaction Mechanism	13
3	Species Used in the Atkinson et al. (1982) Reaction Mechanism	17
4	Definition of the Demerjian (1982) Reaction Mechanism	19
5	Species Used in the Demerjian (1982) Reaction Mechanism	21
6	Definition of the Dodge (1977) Reaction Mechanism	22
7	Species Used in the Dodge (1977) Reaction Mechanism	24
8	Definition of the Killus and Whitten (1982) Reaction Mechanism	25
9	Species Used in the Killus and Whitten (1982) Reaction Mechanism	28
10	Definition of the McRae and Seinfeld (1983) Reaction Mechanism	30
11	Species Used in the McRae and Seinfeld (1983) Reaction Mechanism	33
12	Definition of the Penner and Walton (1982) Reaction Mechanism	34
13	Species Used in the Penner and Walton (1982) Reaction Mechanism	38
14	Representation of Carbonyl Chemistry by Lumped Mechanism	44
15	Representation of Alkane Chemistry by Lumped Mechanism	60
16	Alkene-O Reactions in the Lumped Mechanisms	65
17	Alkene-OH Reactions in the Lumped Mechanisms	66
18	Alkoxy and Hydroxy Alkoxy Radical Reactions Interpreted According to $RO \longrightarrow b_1HO_2^{\cdot} + (1-b_1)RO_2^{\cdot} + b_2HCHO + b_3RCHO$	70
19	Alkene-O ₃ Reactions in the Lumped Mechanisms	76
20	Summary of Photolysis Reaction Steps from Mechanism Survey	94
21	Nitrogen Dioxide Photolysis Rate as a Function of Zenith Angle	100
22	Photolysis Reaction Steps in the Atkinson et al. (1982) Photochemical Reaction Mechanism	104

23	Photolysis Scaling Ratios Relative to NO ₂ Rate for the Atkinson et al. (1982) Photochemical Reaction Mechanism	107
24	Photolysis Reaction Steps in the Killus and Whitten (1982a) Photochemical Reaction Mechanism	109
25	Photolysis Reaction Steps in the McRae and Seinfeld (1983) Photochemical Reaction Mechanism	110
26	Photolysis Reaction Steps in the Dodge (1977) Photochemical Reaction Mechanism	111
27	Photolysis Reaction Steps in the Demerjian (1982) Photochemical Reaction Mechanism	112
28	Photolysis Reaction Steps in the Penner and Walton (1982) Photochemical Reaction Mechanism	113
29	Calculated Ground Level Values of the Photolysis Rate Constants of Key Species as a Function of the Solar Zenith Angle for the Penner and Walton (1982) Photochemical Reaction Mechanism	116
30	Comparison of Key Photolysis Steps Used in Different Photochemical Reaction Mechanisms	117
31	Uncertainty Estimates for Photolysis Steps	119
32	Number of Hydrocarbon Classes and Lumping Procedures Used in the Reaction Mechanism Survey	121
33	Definition of Hydrocarbon Classes in the Atkinson et al. (1982) Photochemical Reaction Mechanism	122
34	Definition of Organic Classes in the Demerjian (1982) Photochemical Reaction Mechanism	123
35	Definition of Organic Classes in the Dodge (1977) Photochemical Reaction Mechanism	124
36	Definition of Organic Classes in the Killus and Whitten (1982ab) Photochemical Reaction Mechanism	125

37	Definition of Organic Classes in the McRae and Seinfeld (1983) Photochemical Reaction Mechanism	126
38	Definition of Organic Classes in the Penner and Walton (1982) Photochemical Reaction Mechanism	127
39	Classification of Organic Species into Lumped Classes for the Smog Chamber Experiment SUR-119J	128
40	Summary of the Concentrations in Each Lumped Classes for the Smog Chamber Experiment SUR-119J	131
41	Classification of Hydrocarbon Species into Lumped Classes for a Typical Urban Composition Profile	141
42	Summary of the Concentrations in Each Lumped Classes for a Typical Urban Composition Profile	143
43	Comparison of Splitting Factors for Different Reaction Mechanisms	145
44	Hydrocarbon Splitting Factors for McRae and Seinfeld (1983) Mechanism Based on Los Angeles Emissions Inventory for 1974	149

ACKNOWLEDGEMENT

We wish to acknowledge the assistance of: Alan C. Lloyd, Fred Lurmann, Marcia Dodge, Kenneth Demerjian, Kenneth Schere, Gary Whitten, Jim Killus and Joyce Penner for providing computer codes and documentation of their mechanisms. Thanks are also due to Richard Kee of SANDIA Laboratories for supplying a copy of the kinetics solution program CHEMKIN. Appreciation is extended to William P.L. Carter for his assistance.

CHAPTER 1

INTRODUCTION

Over the past ten years or so, a great deal of effort has been devoted to developing chemical reaction mechanisms for photochemical air pollution, and, as a result, several mechanisms exist at the present time. Since the atmosphere contains literally scores of hydrocarbon species, it is virtually impossible to write a reaction mechanism that includes the detailed chemistry of each hydrocarbon species present. Although each mechanism is based, more or less, on the same body of experimental kinetic data, the manner of treatment of the hydrocarbon chemistry varies among them. Because the actual number of hydrocarbon species is, as we have noted, too large for the detailed chemistry of each to be included in a mechanism, it has been necessary to reduce the number of hydrocarbon species to a manageable set by a process referred to as lumping. The manner in which this lumping has been carried out constitutes one of the major differences among existing mechanisms.

The differences among the several existing reaction mechanisms would not be of concern if their predictions were in essential agreement over the range of conditions of interest for atmospheric predictions. It has recently been demonstrated, however, that different mechanisms predict rather different degrees of hydrocarbon and NO_x control to achieve the same level of ozone reduction under identical conditions (Jeffries et al., 1981; Whitten, 1981; Carter et

al., 1982). Because of the necessity of using reaction mechanisms for photochemical smog in determining air pollution control strategies, these results point to a serious need to analyze the fundamental nature of such mechanisms and to understand the key elements of their behavior. Such an analysis is the subject of this work.

Figure 1 depicts the ways in which hydrocarbon lumping has been approached in photochemical smog mechanisms. In the surrogate species approach, typified by the mechanism of Dodge (1977), the entire atmospheric mixture is represented by a small number of surrogate hydrocarbon species. In the mechanism of Dodge (1977), propene and n-butane, together with small quantities of formaldehyde and acetaldehyde, represent the entire atmospheric mix.

The other lumping approaches are indicated in Figure 1. Lumped molecule approaches refer to those in which the atmospheric hydrocarbons are lumped into identifiable molecular species. For example, in the surrogate species lumped molecule approach, certain hydrocarbons serve as surrogate species for an entire group of actual species. For example, n-butane can be used to represent all atmospheric alkanes, and the alkane portion of the full mechanism then consists of the detailed explicit chemistry of n-butane. Thus, a mixture of many alkanes is represented by a comparable concentration of n-butane. A mechanism based on this approach is that of Atkinson et al. (1982). We should point out that the mechanism of Dodge (1977), referred to above, is, in essence, also a surrogate species mechanism. However, the n-butane and propene are not necessarily identified with

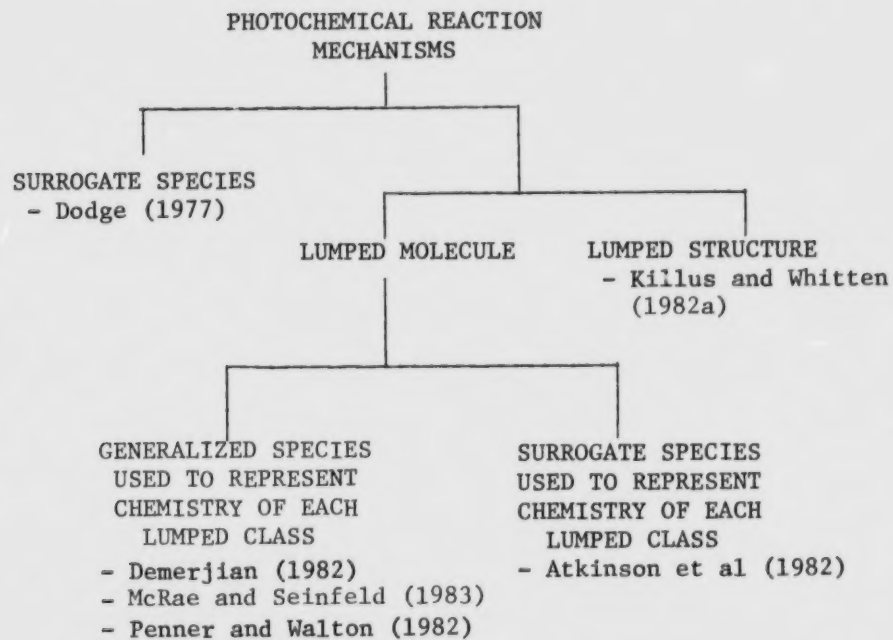


FIGURE 1

Classification of Photochemical Reaction Mechanisms
Used in Evaluation

alkane and alkene species, respectively. Rather, propene and n-butane represent the entire atmospheric mix, where only the total concentration of non-methane hydrocarbons in parts per million by carbon is matched to the initial concentrations of propene and n-butane.

The other type of lumped molecule approach is that of generalized species lumping, in which an entire group of compounds is represented by a generalized species, the chemistry of which reflects the common features of that of the whole group. For example, alkanes could be represented by a species called ALKANE, whose rate constants and reaction mechanisms are, in some manner, an average of those of all alkanes. Mechanisms in this class include those of McRae and Seinfeld (1983), Demerjian (1982), and Penner and Walton (1982).

Finally, in the lumped structure approach, lumped species represent various classes of structural units, such as, single-bonded carbon atoms, double-bonded carbon atoms, and carbonyl carbon atoms. An initial mixture of organics is therefore apportioned by bond type rather than by molecule type to obtain the lumped species. The one mechanism of this type is that of Killus and Whitten (1982a). The Killus and Whitten mechanism, referred to as the Carbon Bond mechanism, treats the reactions of five different types of carbon atoms: 1-alkene carbon atoms except ethene, ethene, single bonded carbon atoms, reactive aromatic rings, carbonyl carbon atoms including carbon atoms from internal olefins.

It is important to point out that any reaction mechanism for the atmospheric chemistry of photochemical smog must involve some aspect of hydrocarbon lumping. It is sometime mistakenly assumed that lumping is not involved in a surrogate mechanism, since a surrogate mechanism consists of the explicit chemistry of the surrogate species. Although the mechanism itself contains only explicit chemical steps, not involving any generalized species, the representation of an atmospheric mixture requires that many species not explicitly included in the mechanism be apportioned to the surrogate species. It is, in fact, the way in which species are apportioned that really constitutes the differences among mechanisms, although mechanisms do differ in the values of rate constants used and in the importance of mechanistic steps where the available experimental information is open to interpretation.

As noted earlier, it has been found that several available photochemical reaction mechanisms do not predict the same ozone levels for the same initial quantities of reactive hydrocarbons and NO_x . Analyzing the behavior of each mechanism is not a straightforward undertaking because of the length of the mechanism (usually between 50 and 100 reactions) and because of the intricate nature of the free radical reaction chains involved. Consequently, it is desirable to employ a technique that enables one to track the complex species flows in a mechanism. Such a method has been developed by Leone and Seinfeld (1983b) and is employed in Part II of this work.

The particular mechanisms chosen for initial testing in this study are shown in Figure 1 and Table 1. Several different criteria were used to select representative mechanisms including: the availability of supporting documentation and the degree of testing against smog chamber experiments. One additional requirement was that each mechanism had to have been implemented in an air quality model and used in emissions control calculations. With this background the following material was requested from each investigator responsible for the development of the reaction mechanism: (1) All the available open and report literature references that describe the scientific basis and testing of the reaction mechanism; (2) A computer listing of the reactions, species names and a duplication of a test case. This latter information was requested to ensure that the mechanism has been implemented in the manner intended by the developer. A summary of the mechanism characteristics, documentation sources and bases for validation is shown in Table 1. The validation bases of the Atkinson et al. (1982), Killus and Whitten (1982a) and Penner and Walton (1982) mechanisms are experiments conducted at the University of California, Riverside, whereas the Demerjian (1982) and Dodge (1977) mechanisms were evaluated on Bureau of Mines smog chamber data. The Killus and Whitten (1982a) mechanism has also been tested against outdoor smog chamber data from the University of North Carolina. Chapter 2 contains summaries of the mechanisms.

Chapter 3 contains a discussion of the basis of the lumping approaches of the five lumped mechanisms: Atkinson et al. (1982),

TABLE 1

Photochemical Reaction Mechanisms Considered for Evaluation -
Their Characteristics and Their Validation Base

REACTION MECHANISM	TYPE ^a	NUMBER OF REACTIONS/ SPECIES	NUMBER OF ORGANIC CLASSES ^b	EXPERIMENT NUMBERS ^c	VALIDATION BASIS TYPE OF EXPERIMENT
Atkinson et al. (1979, 1982) ^c	LM	81/52	14	EC-178	n-butane/NO _x
Carter et al. (1979)				EC-143	ethene/NO _x
Lurmann (1982, 1983)				EC-146	tr-2-butene/NO _x
				EC-216	propene/NO _x
				EC-340	toluene/NO _x
				EC-344	m-xylene/NO _x
				EC-161	4 alkenes/NO _x
				EC-237, EC-242, EC-246	7 hydrocarbons/NO _x
				AGC-119, AGC-133, AGC-134 AGC-135, AGC-138, AGC-150 AGC-156	surrogate (multi- hydrocarbon)/NO _x
				AP-28, AP-30, AP-35, AP-37	hydrocarbon/NO _x /SO ₂
Demerjian (1982) Schere (1983)	LM	45/30	4		40 Bureau of Mines smog chamber experiments with dilute auto exhaust and added NO _x . Several UCR aromatic hydrocarbon/NO _x experiments
Dodge (1977) Durbin et al. (1975)	S	76/39	4		17 Bureau of Mines smog chamber experiments with dilute auto exhaust and added NO _x

Table 1 (continued)

REACTION MECHANISM	TYPE ^a	NUMBER OF REACTIONS/SPECIES	NUMBER OF ORGANIC CLASSES ^b	EXPERIMENT NUMBERS ^c	VALIDATION BASIS TYPE OF EXPERIMENT
Killus and Whitten (1982a) Whitten et al. (1980a,b)	LS	79/41	5	EC-231,EC-232,EC-233, EC-237,EC-238,EC-242, EC-243,EC-245,EC-246, EC-247	7 hydrocarbon/NO _x experiments at SAPRC
				---	2 day urban hydrocarbon mix at UNC
Falls and Seinfeld (1978) ^d Falls et al. (1979) McRae et al. (1982) McRae and Seinfeld (1983)	LM	52/32	6	EC-237 SUR-119J,SUR-121J, SUR-126J,SUR-132J, SUR-133J,SUR-134J	7 hydrocarbon/NO _x surrogate atmospheric mix
Gelinas and Skewes-Cox (1977) MacCracken and Sauter (1975) Penner and Walton (1982)	LM	59/22	4	---	several individual hydrocarbon/NO _x experiments
				EC-231,EC-232,EC-233, EC-237,EC-238,EC-241, EC-242,EC-243,EC-245	7 hydrocarbon/NO _x

Footnotes for Table 1

- (a) The mechanism type refers to: LM - Lumped molecule, S - Surrogate and LS - Lumped structure.
- (b) Number of reactive organic groupings for which either emissions or initial conditions must be specified in practical applications.
- (c) A list of references is provided for each reaction mechanism documenting the evolution, if any, of the mechanism. The mechanism presented here corresponds to that in the most recent reference cited.
- (d) This mechanism was developed by Falls and Seinfeld (1978), with updated rate constants presented by McRae and Seinfeld (1983).
- (e) The experiment numbers refer to the following laboratories:

EC, SUR	Statewide Air Pollution Research Center (SAPRC) of the University of California, Riverside
UNC	University of North Carolina

referred to as ALW, Demerjian (1982), Killus and Whitten (1982), referred to as KW, McRae and Seinfeld (1983), referred to as MS, and Penner and Walton (1982), referred to as PW. Our discussion of the chemistry of photochemical smog is based almost exclusively on the extensive review of Atkinson and Lloyd (1983). Thus, unless otherwise noted, the source of statements concerning individual chemical steps and rate constants in Chapter 3 is that review.

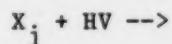
We then examine the specification of photolysis rates (Chapter 4) and initial conditions (Chapter 5) in each of the mechanisms. Chapter 6 contains a summary of the key findings of Part I. Part II of this report is devoted to a detailed evaluation of the characteristics of each of the mechanisms.

CHAPTER 2

DOCUMENTATION AND INITIAL TESTING OF REACTION MECHANISMS

2.1 The Reaction Mechanisms

We now present the detailed mechanisms to be considered in this study. Two tables are used to document each reaction set, the first of which contains the list of elementary reactions. Photolysis steps are denoted by expressions containing the symbol HV i.e.



The second table contains the species names and a set of initial conditions, corresponding to a particular test case that was simulated to ensure that the reaction schemes had been implemented in the manner intended by each investigator. Note that only upper case characters are used to define the species names. They can be directly read by the computer program used to solve the kinetics. Certain species are held at constant concentration during any one experiment. They include water (H2O), molecular oxygen (O2) and M. Each reaction rate constant has been coded with a key that identifies one of four different ways of specifying the rate data.

KEY

RATE CONSTANT FORMAT

-
- 1 $k = A * TEMP^B * EXP(-C/T)$
 - 2 Rate constant specified externally, this form is usually only used for photolysis steps.
 - 3 Rate constant expressed as a proportion of another rate constant so that $K = A * K(B)$ where B identifies the reaction number.
 - 4 For some reactions the rates can be expressed in terms of a zenith angle scaling of another basic rate constant. For example the ozone photolysis rate could be defined as a zenith angle scaling of the NO_2 rate so that $k(O_3+H_2O+h\nu) = D(Z) * K(NO_2+h\nu)$.
-

The units used to specify the rate constants, initial conditions and species concentrations are based on the ppm-min system. In some cases the reaction rate constants have been derived from literature values that have been reported in terms of cm-molecule-sec units. The formulae used for converting first, second and third order rate constants are:

$$k(\text{min}^{-1}) = 60.0 k(\text{sec}) \quad (2.1)$$

$$k(\text{ppm}^{-1}\text{-min}^{-1}) = 4.40 \times 10^{17} (P/T) k(\text{cm}^3\text{-molecule}^{-1}\text{-sec}^{-1}) \quad (2.2)$$

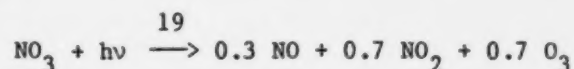
$$k(\text{ppm}^{-2}\text{-min}^{-1}) = 3.23 \times 10^{33} (P/T)^2 k(\text{cm}^6\text{-molecule}^{-2}\text{-sec}^{-1}) \quad (2.3)$$

where P is the pressure in atmospheres and T the temperature in $^{\circ}\text{K}$.

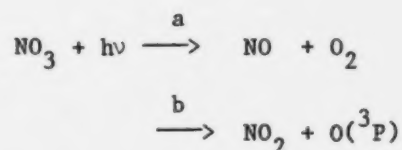
The presence of temperature in the denominators of (2.2) and (2.3) can be treated, in the reaction coding, by including the appropriate exponent B, in the rate constant. Given this background it is now

possible to present the mechanisms considered for detailed evaluation. They are shown in Tables 2 - 13.

A cursory examination of the tables reveals several features of reaction product stoichiometry that deserve further explanation: the presence of non-integer stoichiometric coefficients, negative coefficients for some of the species and individual reactions that appear to violate mass conservation. All of these arise as a result of the need to minimize both the number of species and reactions. There are several ways in which non integer coefficients can arise. For example in the Atkinson et al. (1982) mechanism the photodissociation of nitrogen trioxide is treated as the single step



The composite reaction is the result of combining the two elementary reaction steps



By assuming that the production of molecular oxygen in step a can be ignored and that $\text{O}({}^3\text{P})$ reacts very rapidly through the reaction $\text{O}({}^3\text{P}) + \text{O}_2 + \text{M} \longrightarrow \text{O}_3 + \text{M}$ to form ozone the two pathways can be combined into a single reaction of the form

TABLE 2

Definition of the Atkinson et al. (1982) Reaction Mechanism^a

REACTION ^b	NUMBER	RATE CONSTANT ^c			KEY
		A	B	C	
NO ₂ + HV → NO + O ₃	(01)	0.35	0	0.	2
NO + O ₃ → NO ₂ + O ₂	(02)	1.0E+6	-1	1450.	1
O ₃ + H ₂ O + HV → 2 OH + O ₂	(03)	0.	1	0.	4
OH + NO → HONO	(04)	8.7E+8	-2	0.	1
OH + NO ₂ → HNO ₃	(05)	1.5E+9	-2	0.	1
HONO + HV → OH + NO	(06)	.17	1	0.	3
HO ₂ + NO → OH + NO ₂	(07)	3.7E+6	-1	0.	1
HO ₂ + NO ₂ → HNO ₄	(08)	1.5E+8	-2	0.	1
HNO ₄ → HO ₂ + NO ₂	(09)	7.8E+15	0	10420.	1
HO ₂ + HO ₂ → H ₂ O ₂ + O ₂	(10)	3.4E+4	-1	-1100.	1
HO ₂ + HO ₂ + H ₂ O → H ₂ O ₂ + O ₂	(11)	5.8E-5	-2	-5800.	1
H ₂ O ₂ + HV → 2 OH	(12)	7.1E-4	1	0.	3
OH + CO → HO ₂	(13)	1.3E+5	-1	0.	1
NO ₂ + O ₃ → NO ₃	(14)	5.3E+4	-1	2450.	1
NO + NO ₃ → 2 NO ₂	(15)	8.4E+6	-1	0.	1
NO ₂ + NO ₃ → N ₂ O ₅	(16)	3.1E+7	-1	1100.	1
N ₂ O ₅ → NO ₂ + NO ₃	(17)	3.5E+18	0	12280.	1
N ₂ O ₅ + H ₂ O → 2 HNO ₃	(18)	1.33E-3	-1	0.	1
NO ₃ + HV → 0.3 NO + 0.7 NO ₂ + 0.7 O ₃	(19)	15.5	1	0.	3
OH + O ₃ → HO ₂	(20)	7.0E+5	-1	940.	1
HO ₂ + O ₃ → OH	(21)	4.8E+3	-1	580.	1
HCHO + HV → 2 HO ₂ + CO	(22)	0.	1	0.	4
HCHO + HV → CO + H ₂	(23)	0.	1	0.	4
OH + HCHO → HO ₂ + CO	(24)	4.4E+6	-1	0.	1
ALD ₂ + HV → MPOX + HO ₂ + CO	(25)	0.	1	0.	4
OH + ALD ₂ → ACOX	(26)	3.0E+6	-1	-250.	1
ACOX + NO ₂ → PAN	(26)	2.1E+6	-1	0.	1
PAN → ACOX + NO ₂	(28)	1.2E+18	0	13543.	1
ACOX + NO → NO ₂ + MPOX	(29)	3.1E+6	-1	0.	1
MPOX + NO → HCHO + HO ₂ + NO ₂	(30)	3.1E+6	-1	0.	1
OH + PRPA → PO ₂	(31)	6.6E+6	-1	680.	1
PO ₂ + NO → HO ₂ + NO ₂ + ACET	(32)	3.1E+6	-1	0.	1
OH + ALKA → AO ₂	(33)	6.6E+6	-1	400.	1
AO ₂ + NO → 1.7 NO ₂ + 0.9 HO ₂ + 0.15 HCHO + 0.3 ALD ₂ + 0.1 RCHO + 0.30 ACET + 0.45 MEK - 0.8 NO	(34)	3.1E+6	-1	0.	1
OH + RCHO → RCO ₃	(35)	9.2E+6	-1	0.	1
RCO ₃ + NO ₂ → PPN	(36)	2.1E+6	-1	0.	1
PPN → RCO ₃ + NO ₂	(37)	1.2E+18	0	13543.	1
RCO ₃ + NO → ET ₂ O ₂ + NO ₂	(38)	3.1E+6	-1	0.	1
ET ₂ O ₂ + NO → ALD ₂ + HO ₂ + NO ₂	(39)	3.1E+6	-1	0.	1
RCHO + HV → ET ₂ O ₂ + CO + HO ₂	(40)	8.4E-4	1	0.	3
OH + MEK → XO ₂	(41)	4.4E+6	-1	330.	1

TABLE 2 (Continued)

REACTION ^b	NUMBER	RATE CONSTANT ^c			KEY
		A	B	C	
XO2 + NO --> NO2 + ALD2 + ACOX	(42)	3.1E+6	-1	0.	1
MEK + HV --> ACOX + ETO2	(43)	1.7E-3	1	0.	3
ACET + HV --> ACOX + MPOX	(44)	1.7E-4	1	0.	3
OH + ETHE --> NO2 + HO2 + 2.0 HCHO - 1.0 NO	(45)	9.7E+5	-1	-380.	1
OH + PRPE --> NO2 + HO2 + 1.0 HCHO + 1.0 ALD2 - 1.0 NO	(46)	1.8E+6	-1	-540.	1
OH + BUTE --> 0.9 NO2 + 0.9 HO2 + 1.8 ALD2 - 1.0 NO	(47)	5.0E+6	-1	-540.	1
O3 + ETHE --> HCHO + 0.4 CHO2 + 0.4 CO + 0.12 HO2	(48)	4.2E+3	-1	2560.	1
O3 + PRPE --> 0.5 HCHO + 0.5 ALD2 + 0.2 CHO2 + 0.2 CD + 0.3 CO + 0.2 HO2 + 0.1 OH + 0.2 MPOX	(49)	3.1E+3	-1	1900.	1
O3 + BUTE --> ALD2 + 0.40 CD + 0.3 HO2 + 0.2 OH + 0.45 MPOX + 0.2 CO	(50)	3.3E+3	-1	1050.	1
CHO2 + NO --> HCHO + NO2	(51)	3.1E+6	-1	0.	1
CHO2 + NO2 --> HCHO + NO3	(52)	3.1E+5	-1	0.	1
CHO2 + H2O --> PROD	(53)	1.5E+0	-1	0.	1
CD + NO --> ALD2 + NO2	(54)	3.1E+6	-1	0.	1
CD + NO2 --> ALD2 + NO3	(55)	3.1E+5	-1	0.	1
CD + H2O --> PROD	(56)	1.5E+0	-1	0.	1
OH + BENZ --> 0.25 CRES + 0.25 HO2 + 0.75 ADD	(57)	5.3E+5	-1	0.	1
OH + TOLU --> 0.15 ARO2 + 0.20 CRES + 0.65 ADD + 0.20 HO2	(58)	2.7E+6	-1	0.	1
OH + XYEN --> 0.25 CRES + 0.25 HO2 + 0.75 ADD	(59)	7.9E+6	-1	0.	1
ADD + NO --> 0.75 NO2 + 0.75 HO2 + 0.75 DIAL + B01*GLY + B02*MGLY	(60)	3.1E+6	-1	0.	1
OH + DIAL --> EL	(61)	1.3E+7	-1	0.	1
EL + NO2 --> ENO2	(62)	2.1E+6	-1	0.	1
ENO2 --> EL + NO2	(63)	1.2E+18	0	13543.	1
EL + NO --> 3 NO2 - 2 NO + B03*HO2+B03*GLY + B04*ACOX + B04*MGLY + B03*CO	(64)	3.1E+6	-1	0.	1
OH + GLY --> HO2 + CO	(65)	8.8E+6	-1	0.	1
GLY + HV --> HCHO + CO	(66)	1.E-10	1	0.	3
OH + MGLY --> ACOX + CO	(67)	6.6E+6	-1	0.	1
MGLY + HV --> ACOX + HO2 + CO	(68)	0.15	1	0.	3
OH + CRES --> ADD2	(69)	1.9E+7	-1	0.	1
ADD2 + NO --> 0.75 NO2 + 0.75 HO2 + 0.75 DIAL	(70)	3.1E+6	-1	0.	1
NO3 + CRES --> HNO3 + PHEN	(71)	6.6E+6	-1	0.	1
PHEN + NO2 --> PRODN	(72)	6.6E+6	-1	0.	1
ARO2 + NO --> 0.75 NO2 + 0.75 HO2 + 0.75 ACHO	(73)	3.1E+6	-1	0.	1
ACHO + HV --> PROD	(74)	4.5E-3	1	0.	3
ACHO + OH --> ARC3	(75)	5.7E+6	-1	0.	1
ARC3 + NO2 --> PBZN	(76)	2.1E+6	-1	0.	1

TABLE 2 (Continued)

REACTION ^b	NUMBER	RATE CONSTANT ^c			KEY
		A	B	C	
PBZN --> ARC3 + NO2	(77)	1.0E+17	0	13025.	1
ARC3 + NO --> PHO2 + NO2	(78)	3.1E+6	-1	0.	1
PHO2 + NO --> PHEN + NO2	(79)	3.1E+6	-1	0.	1
:					
:	Wall source terms for OH production and O3 loss				
:					
CONE --> OH	(80)	4.0E-4	0	0.	1
O3 --> WALL	(81)	1.7E-3	0	0.	1

Footnotes for Table 2

(a) Mechanism documentation: Atkinson et al.(1979, 1982), Carter et al.(1979)
 A computer tape containing the reaction mechanism was obtained
 from F. Lurmann, Environmental Research and Technology, Inc.,
 Westlake Villiage, California, on 8 July 1982.

(b) In two reactions (60,64) the product stoichiometry varies as
 a function concentration. The functional forms for the coefficients
 B01, B02, B03 and B04 are given by:

$$B01 = 0.75 * (K(57) * BENZ + 0.1 * K(59) * XYEN) / \\ (K(57) * BENZ + K(58) * TOLU + K(59) * XYEN)$$

$$B03 = (K(57) * BENZ + K(58) * TOLU + 0.5 * K(59) * XYEN) / \\ (K(57) * BENZ + K(58) * TOLU + K(59) * XYEN)$$

$$B02 = 0.75 - B01$$

$$B04 = 1.0 - B03$$

In these expressions, BENZ, TOLU and XYEN are the species
 concentrations and K(57), K(58) and K(59) are rate constants.

Footnotes for Table 2 (Continued)

- (c) Reaction rate constants are of the form $k = A * TEMP^B * \exp(-C/TEMP)$ with units in terms of the ppm-min system. The scaling coefficients for the photolysis reactions 3, 22, 23 and 25 are given in the accompanying table.

SCALING FACTORS D(Z) FOR PHOTOLYSIS RATES RELATIVE TO NO₂

Zenith Angle - Z°	03 O3+H2O+hv -->	22 HCHO+hv -->	23 HCHO+hv -->	25 ALD2+hv -->
0	4.20E-8	0.0035	0.0034	8.4E-4
10	4.10E-8	0.0035	0.0034	8.3E-4
20	3.80E-8	0.0034	0.0034	8.0E-4
30	3.30E-8	0.0033	0.0033	7.4E-4
40	2.60E-8	0.0033	0.0032	6.7E-4
50	1.90E-8	0.0028	0.0030	5.6E-4
60	1.20E-8	0.0024	0.0028	4.4E-4
70	6.20E-9	0.0019	0.0025	3.1E-4
78	3.00E-9	0.0016	0.0022	2.1E-4
84	1.30E-9	0.0014	0.0022	1.3E-4

TABLE 3

Species Used in the Atkinson et al. (1982) Reaction Mechanism

NUMBER	CODE	I.C. ^a	SPECIES NAME
1	ACET		Acetone
2	ACHO		Benzaldehyde
3	ACOX		CH ₃ CO ₃
4	ADD		OH-Aromatic-O ₂ adducts
5	ADD2		OH-Aromatic-O ₂ adducts
6	ALD2		Acetaldehyde
7	ALKA	1.488	>C3 alkanes
8	AO2		Alkyl peroxy radical
9	ARO2		Aromatic peroxy radical
10	ARC3		Peroxy benzoyl
11	BENZ		Benzene
12	BUTE	0.050	>C3 alkenes
13	CD		CH ₃ CHOO
14	CHO2		CH ₂ O ₂
15	CO		Carbon monoxide
15	CONE	1.0	Wall source term for OH
17	CRES		Cresol
18	DIAL		Conjugated gamma dicarbonyls
19	EL		Radical formed from DIAL
20	ENO2		PAN analog from -dicarbonyls
21	ETHE	0.875	Ethylene
22	ETO2		C ₂ H ₅ O ₂
23	GLY		Glyoxal
24	HCHO		Formaldehyde
25	HNO3		Nitric acid
26	HNO4		Pernitric acid
27	HONO		Nitrous acid
28	HO2		Hydroperoxyl radical
29	H2O	23480.0	Water vapor
30	H2O2		Hydrogen peroxide
31	MEK		Methylethylketone
32	MGLY		Methylglyoxal
33	MPOX		Methyl peroxy radical (CH ₃ O ₂)
34	NO	0.377	Nitric oxide
35	NO2	0.106	Nitrogen dioxide
36	NO3		Nitrogen trioxide
37	N2O5		Nitrogen pentoxide
38	OH		Hydroxyl radical
39	O3	0.0001	Ozone
40	PAN		Peroxyacetyl nitrate
41	PBZN		Peroxy Benzoyl nitrate
42	PHEN		Phenoxy Radical
43	PHO2		C ₆ H ₅ O ₂ Radical
44	PO2		Propoxy Radical

TABLE 3 (Continued)

NUMBER	CODE	I.C. ^a	SPECIES NAME
45	PPN		Higher PANS
46	PRPA		Propane
47	PRPE	0.100	Propylene
48	RCHO		C3-C5 aldehydes
49	RCO3		Acylperoxy
50	TOLU	0.086	Toluene
51	XO2		Peroxy radical
52	XYEN	0.091	>C7 aromatics

Footnotes for Table 3

- (a) The initial conditions correspond to smog chamber experiment number EC-237 carried out at the University of California Riverside. The additional information needed to specify the experiment is given by

Dilution Rate = 0.0003 min^{-1}
 Chamber Temperature = 302.0°K

TABLE 4

Definition of the Demerjian (1982) Reaction Mechanism^a

REACTION	NUMBER	RATE CONSTANT ^b			KEY
		A	B	C	
NO2 + HV --> NO + O	(01)	0.35E+0	0	0.	2
O2 + O + M --> O3 + M	(02)	3.90E-6	0	-510.	1
O3 + NO --> NO2 + O2	(03)	3.40E+3	0	1450.	1
O3 + NO2 --> NO3 + O2	(04)	1.77E+2	0	2450.	1
O3 + HV --> O1D + O2	(05)	6.57E-4	0	0.	2
O1D + M --> O + M	(06)	6.68E+4	0	0.	1
O1D + H2O --> 2 OH	(07)	4.14E+5	0	0.	1
NO3 + NO --> 2 NO2	(08)	2.96E+4	0	0.	1
NO3 + NO2 --> N2O5	(09)	1.36E+16	-4.6	0.	1
N2O5 --> NO3 + NO2	(10)	1.30E+16	0	9700.	1
N2O5 + H2O --> 2 HNO3	(11)	1.92E-5	0	0.	1
HONO + HV --> HO + NO	(12)	6.10E-2	0	0.	2
HO + CO --> HO2 + CO2	(13)	4.10E+2	0	0.	1
HO2 + NO2 --> HONO + O2	(14)	4.40E+0	0	0.	1
HO2 + NO --> HO + NO2	(15)	6.36E+3	0	-200.	1
HO2 + NO2 + M --> HO4N + M	(16)	2.63E-3	0	0.	1
HO4N --> HO2 + NO2	(17)	5.21E+15	0	10420.	1
HO + HONO --> NO2 + H2O	(18)	9.75E+3	0	0.	1
HO + NO2 + M --> HNO3 + M	(19)	1.54E-2	0	0.	1
HO + NO + M --> HONO + M	(20)	7.39E-3	0	0.	1
HO + HNO3 --> H2O + NO3	(21)	1.26E+2	0	0.	1
HO2 + O3 --> HO + 2 O2	(22)	2.07E+1	0	600.	1
HO + O3 --> HO2 + O2	(23)	2.81E+3	0	1000.	1
HO2 + HO2 --> H2O2 + O2	(24)	3.40E+3	0	0.	1
H2O2 + HV --> 2 HO	(25)	2.64E-4	0	0.	2
HC1 + O --> RO2 + HC3 + HO2	(26)	5.10E+3	0	0.	1
HC1 + O3 --> RO2 + HC3 + HO2	(27)	1.40E-2	0	0.	1
HC1 + HO --> RO2 + HC3	(28)	3.10E+4	0	0.	1
HC2 + HO --> RO2	(29)	5.00E+3	0	0.	1
HC3 + HV --> 0.5 RO2 + 1.5 HO2 + CO	(30)	1.02E-3	0	0.	2
HC3 + HO --> 0.3 R1O2 + 0.7 HO2 + 0.7 CO	(31)	1.35E+4	0	0.	1
RO2 + NO --> RO + NO2	(32)	1.10E+4	0	0.	1
RO + O2 --> HC3 + HO2	(33)	7.39E+2	0	2000.	1
R1O2 + NO2 --> PAN	(34)	2.07E+3	0	0.	1
PAN --> R1O2 + NO2	(35)	4.77E+16	0	12516.	1
RO + NO2 --> RNO3	(36)	1.00E+2	0	0.	1
RO2 + O3 --> RO + 2 O2	(37)	2.00E+0	0	0.	1
R1O2 + NO --> RO2 + NO2	(38)	4.00E+3	0	0.	1
HC4 + HO --> R2O2 + 2 HC3 + CO	(39)	2.30E+4	0	0.	1
R2O2 + NO --> R2O + NO2	(40)	1.10E+4	0	0.	1
R2O + O2 --> HC3 + HO2 + 2 CO	(41)	8.87E-1	0	0.	1
R2O2 + O3 --> R2O + 2 O2	(42)	2.00E+0	0	0.	1

TABLE 4 (Continued)

REACTION ^b	NUMBER	RATE CONSTANT ^c			KEY
		A	B	C	
R102 + O3 --> RO2 + 2 O2	(43)	2.00E+0	0	0.	1
HC3 + HV --> CO	(44)	1.11E-3	0	0.	2
HC1 + O3 --> COOH + HC3	(45)	1.50E-3	0	0.	1

Footnotes for Table 4

- (a) Mechanism Documentation: Demerjian (1982) and Schere (1983)
 A computer tape containing the reaction mechanism was obtained from K. Schere, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, on 16 June 1982.
- (b) Reaction rate constants are of the form $k = A * TEMP^B * \exp(-C/TEMP)$ with units in terms of the ppm-min system

TABLE 5

Species Used in the Demerji (1982) Reaction Mechanism

NUMBER	CODE	I.C. ^a	SPECIES NAME
1	CO	2.0	Carbon monoxide
2	COOH		Criegee intermediate
3	CO2	320.0	Carbon dioxide
4	HC1	0.038	Olefins including C2H4
5	HC2	0.0459	Alkanes (excluding methane)
6	HC3	0.0230	Aldehydes
7	HC4	0.0237	Aromatics
8	HNO3		Nitric acid
9	HO		Hydroxyl radical
10	HO4N		Pernitric acid
11	HONO	0.006	Nitrous acid
12	HO2		Hydroperoxyl radical
13	H2O	20000.0	Water vapor
14	H2O2	0.000001	Hydrogen peroxide
15	M	1.0E+06	Third body for deactivation
16	NO	0.225	Nitric oxide
17	NO2	0.040	Nitrogen dioxide
18	NO3		Nitrogen trioxide (nitrate radical)
19	N2O5		Nitrogen pentoxide
20	O		Atomic oxygen
21	O1D		Singlet D oxygen
22	O2	2.1E+05	Molecular oxygen
23	O3		Ozone
24	PAN		Peroxyacetylnitrate
25	RNO3		Alkyl nitrate
26	RO		Alkoxy radical
27	RO2		Alkylperoxy radical
28	RI02		Peroxyacyl radical
29	R2O		Alkoxy radical
30	R2O2		Peroxy radical

Footnotes for Table 5

- (a) The initial conditions correspond to smog chamber experiment number 4LUMP-HC carried out by the Bureau of Mines. The additional data needed to characterize the experimental conditions are:

$$\begin{aligned} \text{Dilution Rate} &= 0.000383 \text{ min}^{-1} \\ \text{Chamber Temperature} &= 306.5 \text{ }^{\circ}\text{K} \end{aligned}$$

TABLE 6

Definition of the Dodge (1977) Reaction Mechanism

REACTION	NUMBER	RATE CONSTANT ^b			KEY
		A	B	C	
NO ₂ + HV → NO + O	(1)	0.35	0	0.	2
O + O ₂ + M → O ₃ + M	(2)	2.0E-5	0	0.	1
NO + O ₃ → NO ₂	(3)	25.0	0	0.	1
O ₃ + NO ₂ → NO ₃	(4)	0.045	0	0.	1
O + NO ₂ → NO	(5)	1.3E+4	0	0.	1
NO + NO ₃ → 2 NO ₂	(6)	1.3E+4	0	0.	1
NO ₃ + NO ₂ → N ₂ O ₅	(7)	5.6E+3	0	0.	1
N ₂ O ₅ → NO ₂ + NO ₃	(8)	22.0	0	0.	1
H ₂ O + N ₂ O ₅ → 2 HONO	(9)	2.5E-6	0	0.	1
NO ₂ + NO + H ₂ O → 2 HONO	(10)	1.0E-9	0	0.	1
HONO + HONO → NO + NO ₂	(11)	1.0E-3	0	0.	1
HONO + HV → OH + NO	(12)	6.3E-3	0	0.	2
NO ₂ + OH → HNO ₃	(13)	8.0E+3	0	0.	1
NO + OH → HONO	(14)	3.0E+3	0	0.	1
NO + HO ₂ → NO ₂ + OH	(15)	1.2E+3	0	0.	1
HO ₂ + HO ₂ → HOOH + O ₂	(16)	8.4E+3	0	0.	1
HOOH + HV → 2 OH	(17)	8.4E-4	0	0.	2
O ₃ + HV → O ¹ D	(18)	9.5E-4	0	0.	2
O ₃ + HV → O	(19)	1.9E-2	0	0.	2
O ¹ D + M → O + M	(20)	8.7E+4	0	0.	1
O ¹ D + H ₂ O → 2 OH	(21)	5.1E+5	0	0.	1
O ₃ + OH → HO ₂ + O ₂	(22)	84.0	0	0.	1
HO ₂ + O ₃ → OH	(23)	2.4	0	0.	1
OH + PROP → ADD	(24)	2.5E+4	0	0.	1
NO + ADD → X + NO ₂	(25)	1.0E+3	0	0.	1
ADD + ADD → 2 X	(26)	1.2E+4	0	0.	1
ME ₂ O + ADD → X + ME ₂ O	(27)	1.0E+3	0	0.	1
C ₂ O ₂ + ADD → X + C ₂ O	(28)	1.0E+3	0	0.	1
C ₃ O ₂ + ADD → X + C ₃ O	(29)	1.0E+3	0	0.	1
X → HCHO + ALD ₂ + HO ₂	(30)	1.0E+5	0	0.	1
O ₃ + PROP → OH + HO ₂ + ALD ₂	(31)	8.0E-3	0	0.	1
O ₃ + PROP → OH + C ₂ O ₃ + HCHO	(32)	8.0E-3	0	0.	1
OH + BUT → SC ₂ O ₂	(33)	1.8E+3	0	0.	1
OH + BUT → C ₄ O ₂	(34)	1.8E+3	0	0.	1
C ₄ O ₂ + NO → NO ₂ + C ₄ O	(35)	1.8E+3	0	0.	1
SC ₂ O ₂ + NO → NO ₂ + SC ₂ O	(36)	1.8E+3	0	0.	1
C ₃ O ₂ + NO → NO ₂ + C ₃ O	(37)	1.8E+3	0	0.	1
C ₂ O ₂ + NO → NO ₂ + C ₂ O	(38)	1.8E+3	0	0.	1
ME ₂ O + NO → NO ₂ + ME ₂ O	(39)	1.8E+3	0	0.	1
C ₄ O → HCHO + C ₃ O ₂	(40)	7.5E+4	0	0.	1
SC ₂ O → ALD ₂ + C ₂ O ₂	(41)	1.0E+5	0	0.	1
C ₃ O → HCHO + C ₂ O ₂	(42)	8.0E+3	0	0.	1

TABLE 6 (Continued)

REACTION	NUMBER	RATE CONSTANT ^b			KEY
		A	B	C	
C2O --> HCHO + ME02	(43)	4.0E+3	0	0.	1
C40 + O2 --> ALD4 + HO2	(44)	0.7	0	0.	1
SC0 + O2 --> MEK + HO2	(45)	1.4	0	0.	1
C30 + O2 --> ALD3 + HO2	(46)	0.5	0	0.	1
C20 + O2 --> ALD2 + HO2	(47)	0.4	0	0.	1
ME0 + O2 --> HCHO + HO2	(48)	0.4	0	0.	1
HCHO + HV --> PROD	(49)	3.0E-3	0	0.	2
HCHO + HV --> 2 HO2	(50)	1.0E-3	0	0.	2
OH + HCHO --> HO2 + CO	(51)	1.5E+4	0	0.	1
ALD2 + HV --> PROD	(52)	4.2E-6	0	0.	2
ALD2 + HV --> ME02 + HO2	(53)	9.8E-4	0	0.	2
OH + ALD2 --> C203	(54)	1.5E+4	0	0.	1
ALD3 + HV --> PROD	(55)	6.0E-5	0	0.	1
ALD3 + HV --> C202 + HO2	(56)	2.5E-3	0	0.	1
OH + ALD3 --> C303	(57)	4.5E+4	0	0.	1
ALD4 + HV --> PROD	(58)	6.0E-5	0	0.	1
ALD4 + HV --> C302 + HO2	(59)	1.9E-3	0	0.	1
OH + ALD4 --> C403	(60)	4.5E+4	0	0.	1
C402 + ADD --> X + C40	(61)	1.0E+3	0	0.	1
SC02 + ADD --> X + SC0	(62)	1.0E+3	0	0.	1
NO + C403 --> C302 + NO2	(63)	8.0E+2	0	0.	1
NO + C303 --> C203 + NO2	(64)	8.0E+2	0	0.	1
NO + C203 --> ME02 + NO2	(65)	8.0E+2	0	0.	1
NO2 + C403 --> PAN	(66)	1.0E+2	0	0.	1
NO2 + C303 --> PAN	(67)	1.0E+2	0	0.	1
NO2 + C203 --> PAN	(68)	1.0E+2	0	0.	1
HO2 + C402 --> PROD	(69)	4.0E+3	0	0.	1
HO2 + C302 --> PROD	(70)	4.0E+3	0	0.	1
HO2 + SC02 --> PROD	(71)	4.0E+3	0	0.	1
HO2 + C202 --> PROD	(72)	4.0E+3	0	0.	1
HO2 + ME02 --> PROD	(73)	4.0E+3	0	0.	1
HO2 + C403 --> PROD	(74)	4.0E+3	0	0.	1
HO2 + C303 --> PROD	(75)	4.0E+3	0	0.	1
HO2 + C203 --> PROD	(76)	4.0E+3	0	0.	1

Footnotes for Table 6

(a) Mechanism Documentation: Dodge (1977) and Durbin et al. (1975)

The actual coding for the reactions and the rate constants were derived from the computer program: OZIPP - Isopleth Plotting Plotting Program obtained from H.L. Jeffries on 20 November 1982.

(b) Reaction rate constants are of the form $k = A * TEMP^B * \exp(-C/TEMP)$ with units in terms of the ppm-min system

TABLE 7

Species Used in the Dodge (1977) Reaction Mechanism

NUMBER	CODE	I.C. ^a	SPECIES NAME
1	ADD		CH ₃ CH(OH)CH ₂ OO
2	ALD2	0.012	CH ₃ CHO
3	ALD3		CH ₃ CH ₂ CHO
4	ALD4		CH ₃ CH ₂ CH ₂ CHO
5	BUT	0.1238	n-Butane (n-C ₄ H ₁₀)
6	C2O		CH ₃ CH ₂ O
7	C2O2		CH ₃ CH ₂ O ₂
8	C2O3		CH ₃ C(O)O ₂
9	C3O		CH ₃ CH ₂ CH ₂ O
10	C3O2		CH ₃ CH ₂ CH ₂ O ₂
11	C3O3		CH ₃ CH ₂ C(O)O ₂
12	C4O		CH ₃ CH ₂ CH ₂ CH ₂ O
13	C4O2		CH ₃ CH ₂ CH ₂ CH ₂ O ₂
14	C4O3		CH ₃ CH ₂ CH ₂ C(O)O ₂
15	HCHO	0.018	Formaldehyde
16	HNO3		Nitric acid
17	HONO	0.006	Nitrous acid
18	HO2		Hydroperoxyl radical
19	H2O	20000	Water vapor
20	HOOH		Hydrogen peroxide
21	M	1.0E+06	Third body
22	MEK		Methyl ethyl ketone
23	MEO		Methoxy radical
24	MEO2		Methyl peroxy radical
25	NO	0.225	Nitric oxide
26	NO2	0.040	Nitrogen dioxide
27	NO3		Nitrogen trioxide (nitrate radical)
28	N2O5		Nitrogen pentoxide
29	O		Atomic oxygen O(³ P)
30	OH		Hydroxyl radical
31	OID		Singlet D oxygen
32	O2	2.1E+05	Molecular oxygen
33	O3		Ozone
34	PAN		Peroxyacetyl nitrate
35	PROP	0.055	Propylene
36	SCO		CH ₃ CH(O)CH ₂ CH ₃
37	SCO2		CH ₃ CH(O ₂)CH ₂ CH ₃
38	PROD		Stable products
39	X		CH ₃ CH(OH)CH ₂ O

Footnotes for Table 7

(a) Same conditions as Table 5.

TABLE 8

Definition of the Killus and Whitten (1982a) Reaction Mechanism^a

REACTION	NUMBER	RATE CONSTANT ^b			KEY
		A	B	C	
NO ₂ + HV → NO + O	(1)	0.30	0	0.	2
0 → O ₃	(2)	4.40E+6	0	0.	1
NO + O ₃ → NO ₂ + O ₂	(3)	3.45E+3	0	1450.	1
NO ₂ + O ₃ → NO ₃ + O ₂	(4)	1.79E+2	0	2450.	1
NO ₂ + O → NO + O ₂	(5)	1.34E+4	0	0.	1
O ₃ + OH → HO ₂ + O ₂	(6)	2.87E+1	0	1000.	1
O ₃ + HO ₂ → OH + 2 O ₂	(7)	4.01E+2	0	1525.	1
OH + NO ₂ → HNO ₃	(8)	1.60E+4	0	0.	1
OH + CO → HO ₂	(9)	4.40E+2	0	0.	1
NO + NO → 2 NO ₂	(10)	1.50E-4	0	0.	1
NO + NO ₃ → 2 NO ₂	(11)	2.80E+4	0	0.	1
NO ₃ + NO ₂ + H ₂ O → 2 HNO ₃	(12)	5.56E-19	0	-10600.	1
NO + HO ₂ → NO ₂ + OH	(13)	1.20E+4	0	0.	1
HO ₂ HO ₂ → H ₂ O ₂ + O ₂	(14)	1.50E+4	0	0.	1
X + PAR →	(15)	1.00E+5	0	0.	1
OH + PAR → ME ₂ O + H ₂ O	(16)	8.51E+3	0	560.	1
O + OLE → ME ₂ O + AC ₃ O + X	(17)	8.04E+3	0	325.	1
O + OLE → CARB + PAR	(18)	8.04E+3	0	325.	1
OH + OLE → RA ₂ O	(19)	6.04E+3	0	-540.	1
O ₃ + OLE → CARB + CRIG	(20)	4.70	0	1900.	1
O ₃ + OLE → CARB + MCRG + X	(21)	4.70	0	1900.	1
O + ETH → ME ₂ O + HO ₂ + CO	(22)	8.79E+3	0	800.	1
O + ETH → CARB + PAR	(23)	8.79E+3	0	800.	1
OH + ETH → RBO ₂	(24)	3.33E+3	0	-382.	1
O ₃ + ETH → CARB + CRIG	(25)	1.29E+1	0	2560.	1
NO + AC ₃ O → NO ₂ + ME ₂ O + CO ₂	(26)	1.04E+4	0	0.	1
NO + RBO ₂ → NO ₂ + 2 CARB + HO ₂	(27)	1.20E+4	0	0.	1
NO + RA ₂ O → NO ₂ + 2 CARB + HO ₂	(28)	1.20E+4	0	0.	1
NO + ME ₂ O → NO ₂ + CARB + ME ₂ O + X	(29)	3.80E+3	0	0.	1
NO + ME ₂ O → NO ₂ + CARB + HO ₂	(30)	7.70E+3	0	0.	1
NO + ME ₂ O → NRAT	(31)	5.00E+2	0	0.	1
O ₃ + RBO ₂ → 2 CARB + HO ₂ + O ₂	(32)	5.00	0	0.	1
O ₃ + RA ₂ O → 2 CARB + HO ₂ + O ₂	(33)	2.00E+2	0	0.	1
OH + CARB → CRO ₂ + X	(34)	5.00E+2	0	0.	1
OH + CARB → HO ₂ + CO	(35)	7.00E+3	0	0.	1
OH + CARB → AC ₃ O + X	(36)	6.00E+3	0	0.	1
CARB + HV → CO + H ₂	(37)	1.90E-4	0	0.	2
CARB + HV → 1.333 HO ₂ + CO + 0.667 ME ₂ O + 0.667 X	(38)	3.80E-4	0	0.	2
AC ₃ O + NO ₂ → PAN	(39)	7.00E+3	0	0.	1
PAN → AC ₃ O + NO ₂	(40)	1.04E+18	0	13500.	1
AC ₃ O + HO ₂ → PRD ₁	(41)	1.50E+4	0	0.	1
ME ₂ O + HO ₂ → PRD ₂	(42)	9.00E+3	0	0.	1
NO + CRIG → NO ₂ + CARB	(43)	1.20E+4	0	0.	1

TABLE 8 (Continued)

REACTION	NUMBER	RATE CONSTANT ^b			KEY
		A	B	C	
NO2 + CRIG -->	NO3 + CARB (44)	8.00E+3	0	0.	1
CARB + CRIG -->	OZD (45)	2.00E+3	0	0.	1
NO + MCRG -->	NO2 + CARB (46)	1.20E+4	0	0.	1
NO2 + MCRG -->	NO3 + CARB + PAR (47)	8.00E+3	0	0.	1
CARB + MCRG -->	OZD (48)	2.00E+3	0	0.	1
CRIG -->	CO + H2O (49)	6.70E+2	0	0.	1
CRIG -->	PRD3 (50)	2.40E+2	0	0.	1
CRIG -->	2 HO2 + CO2 (51)	9.00E+1	0	0.	1
MCRG -->	PRD4 (52)	1.50E+2	0	0.	1
MCRG -->	MEO2 + OH + CO (53)	3.40E+2	0	0.	1
MCRG -->	MEO2 + HO2 + CO2 (54)	4.25E+2	0	0.	1
MCRG -->	2 HO2 + CARB + CO (55)	8.50E+1	0	0.	1
ARO + OH -->	RARO + H2O (56)	5.99E+4	0	600.	1
ARO + OH -->	OPEN + HO2 (57)	5.55E+4	0	400.	1
RARO + NO -->	NO2 + PHEN + HO2 (58)	4.00E+3	0	0.	1
OPEN + NO -->	NO2 + DCRB + X + APRC (59)	6.00E+3	0	0.	1
APRC -->	DCRB + CARB + CO + X (60)	1.00E+4	0	0.	1
APRC -->	2 CARB + 2 CO (61)	1.00E+4	0	0.	1
PHEN + NO3 -->	PHO + HNO3 (62)	5.00E+3	0	0.	1
PHO + NO2 -->	NPHN (63)	4.00E+3	0	0.	1
PHO + HO2 -->	PHEN (64)	5.00E+4	0	0.	1
OPEN + O3 -->	DCRB + APRC + X (65)	4.00E+1	0	0.	1
PHEN + OH -->	HO2 + APRC + PAR + CARB (66)	3.00E+4	0	0.	1
DCRB + HV -->	HO2 + 0.5 ACO3 + 1.5 CO + 0.5 ME02 (67)	1.35E-2	0	0.	2
PHEN + OH -->	PHO (68)	1.00E+4	0	0.	1
CRO2 + NO -->	NO2 + CARB + ACO3 + X (69)	1.20E+4	0	0.	1
DCRB + OH -->	ACO3 + CO (70)	7.00E+3	0	0.	1
HONO + HV -->	OH + NO (71)	1.80E-1	0	0.	2
NO + OH -->	HONO (72)	9.77E+3	0	0.	1
O3 + HV -->	OLD (73)	1.00E-3	0	0.	2
OLD -->	O (74)	4.44E+10	0	0.	1
OLD + H2O -->	2 OH (75)	3.40E+5	0	0.	1

TABLE 8 (Continued)

REACTION	NUMBER	RATE CONSTANT ^b			KEY
		A	B	C	
: : Wall loss term for ozone, NO2, NO3, N2O5 :					
03 --> WALL	(76)	1.60E-3	0	0.	1
NO2 + NO3 + H2O --> 2 WNO3	(77)	1.70E-3	0	0.	1
: : Wall source term for NOx :					
--> NO	(78)	1.00E-4	0	0.	1
: : Water production :					
H2O -->	(79)	-6.93E-4	0	0.	1

Footnotes for Table 8

- (a) Mechanism documentation: Killus and Whitten (1982a) and Whitten et al. (1980a,b). The reaction mechanism was coded from Table 3 of Killus and Whitten (1982a) with the photolysis rates and wall terms obtained from a computer listing supplied by J.P. Killus on 25 August 1982. Reactions 26, 48, 54, 60, 69 and 70 have been corrected to maintain the overall carbon balance.
- (b) Reaction rate constants are of the form $k = A * TEMP^B * \exp(-C/TEMP)$ with units in terms of the ppm-min system.

TABLE 9

Species Used in the Killus and Whitten (1982a) Reaction Mechanism

NUMBER	CODE ^a	I.C. ^b	SPECIES NAME
1	AC03 (2)		Peroxyacyl radical (Two-carbon surrogate for RC03)
2	APRC (4)		Conjugated gamma-dicarbonyls
3	ARO (6)	0.229	Reactive aromatic rings
4	CO (1)	1.63	Carbon monoxide
5	CO2 (1)		Carbon dioxide
6	CRIG (1)		Criegee intermediate
7	CRO2 (2)		Peroxy radical
8	DCRB (3)		Highly photolytic alpha-dicarbonyl compounds including methyl glyoxal and biacetyl
9	ETH (2)	1.051	Slow double bonds that are almost exclusively ethylene
10	CARB (1)	0.130	Carbonyl compounds such as aldehydes and ketones
11	HNO3		Nitric acid
12	HONO	0.006	Nitrous acid
13	HO2		Hydroperoxy radical
14	H2		Hydrogen
15	H2O	17000.0	Water vapor
16	H2O2		Hydrogen peroxide
17	MCRG (2)		Criegee intermediate
18	ME02 (1)		Peroxy radical (one-carbon surrogate for R02)
19	NO	0.44	Nitric oxide
20	NO2	0.052	Nitrogen dioxide
21	NO3		Nitrogen trioxide (nitrate radical)
22	NPHN (6)		Nitrophenol
23	NRAT (1)		Nitrate
24	OLE (2)	0.108	Relatively reactive double-bonded carbon molecules
25	O		Atomic oxygen O(3P)
26	OH		Hydroxyl radical
27	OPEN (6)		Bicyclic peroxy radical
28	O1D		Atomic oxygen O(1D)
29	O2	209000.0	Molecular oxygen
30	O3		Ozone
31	OZD (2)		Ozonide
32	OZON (1)		Ozonide
33	PAN (2)		Peroxyacetyl nitrate
34	PAR (1)	9.365	Single-bonded carbon atoms whose principal constituent are paraffinic carbon molecules
35	PHEN (6)		Phenol

TABLE 9 (Continued)

NUMBER	CODE	I.C. ^a	SPECIES NAME
35	PHO (6)		C ₆ H ₅ O Radical
36	RAO2 (2)		Peroxy radical
37	RARO (6)		Peroxy radical
38	RBO2 (2)		Peroxy radical
39	WNO3		Wall loss of NO _x species
40	X (-1)		Species introduced to maintain Carbon balance

Footnotes for Table 9

- (a) The values in brackets are the species carbon numbers
- (b) The initial conditions correspond to smog chamber experiment number EC231 carried out at the University of California Riverside. The additional data needed to characterize the experimental conditions are:

Dilution Rate = 0.000693 min⁻¹
 Chamber Temperature = 303.0 °K

TABLE 10

Definition of the McRae and Seinfeld (1983) Reaction Mechanism^a

REACTION ^b	NUMBER	RATE CONSTANT ^c			KEY
		A	B	C	
NO2 + HV --> NO + O3P	(1)	0.30	0	0.	2
O3P + O2 + M --> O3 + M	(2)	0.346	-2	-510.	1
O3 + NO --> NO2 + O2	(3)	9.24E+05	-1	1450.	1
NO2 + O3P --> NO + O2	(4)	3.99E+06	-1	0.	1
NO + O3P --> NO2	(5)	1.67E+05	-1	-584.	1
NO2 + O3P --> NO3	(6)	1.07E+06	-1	0.	1
O3 + NO2 --> NO3 + O2	(7)	5.19E+04	-1	2450.	1
NO3 + NO --> 2NO2	(8)	8.05E+06	-1	0.	1
NO + OH --> HONO	(9)	5.07E+06	-1	0.	1
HONO + HV --> OH + NO	(10)	0.0548	0	0.	2
HO2 + NO2 --> HONO + O2	(11)	1.73E+01	-1	-1006.	1
HONO + OH --> NO2 + H2O	(12)	2.91E+06	-1	0.	1
NO2 + HO2 --> HO2NO2	(13)	1.73E+04	-1	-1006.	1
HO2NO2 --> HO2 + NO2	(14)	1.80E+15	0	9950.	1
HO2 + NO --> NO2 + OH	(15)	3.58E+06	-1	0.	1
RO2 + NO --> NO2 + RO	(16)	3.58E+06	-1	0.	1
RCO3 + NO --> NO2 + RO2 + CO2	(17)	1.13E+06	-1	0.	1
NO2 + OH --> HONO2	(18)	4.53E+06	-1	0.	1
CO + OH --> HO2 + CO2	(19)	1.31E+05	-1	0.	1
O3 + HV --> O3P + O2	(20)	0.0214	0	0.	2
HCHO + HV --> 2 HO2 + CO	(21)	0.00113	0	0.	2
HCHO + HV --> H2 + CO	(22)	0.00242	0	0.	2
HCHO + OH --> HO2 + H2O + CO	(23)	4.14E+06	-1	0.	1
RCHO + HV --> RO2 + HO2 + CO	(24)	0.00096	0	0.	2
RCHO + OH --> RCO3	(25)	2.57E+04	0	0.	1
C2H4 + OH --> RO2	(26)	1.16E+04	0	0.	1
C2H4 + O3P --> RO2 + HO2	(27)	1.22E+03	0	0.	1
OLE + OH --> RO2	(28)	5.85E+04	0	0.	1
OLE + O3P --> RO2 + RCO3	(29)	9.93E+03	0	0.	1
OLE + O3 --> A01*RCHO + A02*HCHO + A03*HO2 + A04*RO2 + A05*OH + A06*RO	(30)	0.056	0	0.	1
ALK + OH --> RO2	(31)	6.06+03	0	0.	1
ALK + O3P --> RO2 + OH	(32)	99.8	0	0.	1
ARO + OH --> RO2 + RCHO	(33)	2.21E+04	0	0.	1
RO --> B01*HO2 + B02*HCHO + B03*RCHO + B04*RO2	(34)	2.0E+05	0	0.	1
RONO + HV --> NO + RO	(35)	0.066	0	0.	2
RO + NO --> RONO	(36)	4.38E+06	-1	0.	1
RO + NO2 --> RONO2	(37)	2.19E+06	-1	0.	1
RO + NO2 --> RCHO + HONO	(38)	6.39E+02	0	0.	1
NO2 + RO2 --> RO2NO2	(39)	1.64E+06	-1	0.	1
NO2 + RO2 --> RCHO + HONO2	(40)	1.64E+03	-1	0.	1
RO2NO2 --> NO2 + RO2	(41)	1.80E+15	0	9950.	1

TABLE 10 (Continued)

REACTION ^b	NUMBER	RATE CONSTANT ^c			KEY
		A	B	C	
RCO3 + NO2 --> PAN	(42)	6.17E+05	-1	0.	1
PAN --> RCO3 + NO2	(43)	4.77E+16	0	12516.	1
NO2 + NO3 --> N2O5	(44)	2.20E+06	-1	0.	1
N2O5 --> NO2 + NO3	(45)	3.44E+016	0	10600.	1
H2O + N2O5 --> 2 HONO2	(46)	4.47E-03	-1	0.	1
O3 + OH --> HO2 + O2	(47)	6.62E+05	-1	1000.	1
O3 + HO2 --> OH + 2 O2	(48)	4.85E+03	-1	580.	1
O3 --> WALL	(49)	0.0023	0	0.	1
HO2 + HO2 --> H2O2 + O2	(50)	8.28E+03	0	0.	1
H2O2 + HV --> 2 OH	(51)	7.69E-04	0	0.	2
RO2 + RO2 --> 2 RO	(52)	2.04E+04	-1	-223.	1

Footnotes for Table 10

(a) Mechanism documentation: Falls and Seinfeld (1978)
Falls et al. (1979), McRae et al. (1982) and
McRae and Seinfeld (1983). (15 November 1982)

(b) In two reactions (30,34) the product stoichiometry varies as
a function concentration. The functional forms for the
coefficients A01 - A06 and B01-B04 are given by:

$$\begin{array}{lll} A01 = 0.5 & A02 = 0.5 & A03 = 0.304 \\ A04 = 0.306 & A05 = 0.136 & A06 = 0.034 \end{array}$$

and

$$\begin{array}{lll} B01 = 1.0 & B02 = 0.5 & B03 = 0.5 \\ B04 = (1-B01) = 0.0 \end{array}$$

(c) Reaction rate constants are of the form $k = A * TEMP^b * \exp(-C/TEMP)$
with units in terms of the ppm-min system

(d) $k_{37}/(k_{37} + k_{38}) = 0.92$ for CH_3 , $k_{38} = 0.087 k_{37}$

(e) Rate constants for reactions 39 and 40 are based on the assumption
that $k_{16}/(k_{39} + k_{40}) = 2.2$.

(f) Rate constant for reaction 18 determined from

$$1.477 \times 10^{15} \times 10^{-(11.6T/(17.4+T))} \text{SQRT}(280/T)$$

Footnotes for Table 10 (Continued)

(g) Rate constant for reaction 50 determined from

$$k_{50} = \frac{3.4 \times 10^4}{T} \exp(1100/T) + \frac{5.8 \times 10^{-5}}{T^2} \exp(5800/T) [\text{H}_2\text{O}]$$

$$\text{at } 298^\circ\text{K}, [\text{H}_2\text{O} = 20000 \text{ ppm}] \quad k_{50} = 8.28 \times 10^3$$

TABLE 11

Species Used in the McRae and Seinfeld (1983) Reaction Mechanism

NUMBER	CODE	I.C. ^a	SPECIES NAME
1	ALK	1.488	Alkanes (excluding CH ₄)
2	ARO	0.177	Aromatics
3	CO		Carbon monoxide
4	CO ₂		Carbon dioxide
5	ETH	0.875	Ethylene (C ₂ H ₄)
6	HCHO		Formaldehyde
7	HNO ₂	0.01	Nitrous acid
8	HNO ₃		Nitric acid
9	HNO ₄		Pernitric acid
10	HO ₂		Hydroperoxyl radical
11	H ₂		Hydrogen
12	H ₂ O	15500.	Water vapor
13	H ₂ O ₂		Hydrogen peroxide
14	M	1000000.	Third body for collisional deactivation
15	NO	0.377	Nitric oxide
16	NO ₂	0.106	Nitrogen dioxide
17	NO ₃		Nitrogen trioxide
18	N ₂ O ₅		Dinitrogen pentoxide
19	OLE	0.150	Olefins excluding ethylene
20	O		Atomic oxygen (O(3P))
21	OH		Hydroxyl radical
22	O ₂	210000.	Molecular oxygen
23	O ₃		Ozone
24	PAN		Peroxyacetylnitrate
25	RCHO	0.0012	Higher aldehydes
26	RCO ₃		Peroxyacyl radical
27	RO		Alkoxy radical
28	RONO		Alkyl nitrite
29	RNO ₄		Peroxyalkyl nitrate
30	RO ₂		Alkylperoxy radical
31	RNO ₃		Alkyl nitrate
32	WALL		Wall loss term

Footnotes for Table 11

(a) Mechanism documentation: McRae et al.(1982), Falls et al.(1979), Falls and Seinfeld (1978) and McRae and Seinfeld (1983).

(b) The initial conditions correspond to smog chamber experiment number EC - 237 carried out at the University of California Riverside. The additional data needed to characterize the to characterize the experimental conditions are:

Dilution Rate = 0.0003 min⁻¹
 Chamber Temperature = 302.0 °K

TABLE 12

Definition of the Penner and Walton (1982) Reaction Mechanism^a

REACTION	NUMBER	RATE CONSTANT ^b			KEY
		A	B	C	
:					
: Inorganic reactions (R1 - R23)					
:					
O + O2 + M --> O3 + M	(01)	3.90E-6	0	-510.	1
O3 + NO --> NO2 + O2	(02)	1.01E+6	-1	1450.	1
O + NO --> NO2	(03)	1.59E+7	-1.5	0.	1
O + NO2 --> NO + O2	(04)	4.09E+6	-1	0.	1
O + NO2 --> NO3	(05)	2.05E+8	-2	0.	1
O3 + NO2 --> NO3 + O2	(06)	5.28E+4	-1	2450.	1
NO3 + NO2 --> N2O5	(07)	6.05E+4	-0.7	0.	1
N2O5 --> NO2 + NO3	(08)	2.16E+18	-0.7	11180.	1
NO3 + NO --> 2 NO2	(09)	8.80E+6	-1	0.	1
N2O5 + H2O --> 2 HNO3 ^c	(10)	1.32E-3	-1	0.	1
HO + NO2 --> HNO3	(11)	8.67E+7	-1.5	0.	1
HO + NO --> HNO2	(12)	4.99E+7	-1.5	0.	1
HO + CO --> HO2	(13)	1.19E+5	-1	0.	1
HO2 + NO --> HO + NO2	(14)	1.54E+6	-1	-250.	1
HNO2 + HO --> NO2	(26)	2.90E+6	-1	0.	1
HO2 + HO2 --> H2O2 + O2	(27)	3.70E+4	-1	-1250.	1
HO + HO2 --> H2O + O2	(36)	3.52E+7	-1	0.	1
HO + H2O2 --> HO2	(72)	7.04E+5	-1	0.	1
HO + HNO4 --> H2O + NO2 + O2	(93)	1.76E+6	-1	0.	1
HNO4 --> HO2 + NO2	(84)	3.00E+16	0	10720.	1
HO2 + NO2 --> HNO4	(34)	6.23E+15	-5	0.	1
HO + O3 --> HO2	(48)	7.04E+5	-1	940.	1
HO2 + O3 --> HO	(49)	4.84E+3	-1	580.	1
:					
: Reactions of HCl (Alkenes, isoprene and mono-terpenes)					
:					
HCl + HO --> RO2 + HC4	(17)	1.76E+7	-1	120.	1
HCl + O3 --> HO2 + HC4	(16)	1.54E+3	-1	1900.	1
HCl + O3 --> HC4	(47)	1.54E+3	-1	1900.	1
HCl + O --> RO2 + RC03	(15)	4.40E+6	-1	360.	1
HCl + NO3 --> RO2 + RN03	(40)	4.40E+5	-1	1400.	1
:					
: Reactions of HC2 (Alkanes)					
:					
HC2 + HO --> RO2 + H2O	(19)	2.20E+7	-1	900.	1
HC2 + O --> RO2 + HO	(18)	7.04E+6	-1	2000.	1
:					
: Reactions of HC4 (Aldehydes and Ketones)					
:					
HC4 + HO --> RC03 + H2O	(20)	3.52E+6	-1	0.	1
HC4 + HO --> CO + HO2 + H2O	(37)	3.43E+6	-1	150.	1
HC4 + NO3 --> RC03 + HNO3	(35)	1.32E+3	-1	200.	1

TABLE 12 (Continued)

REACTION	NUMBER	RATE CONSTANT ^b			KEY
		A	B	C	
:					
: Reactions of HC3 (Aromatics)					
:					
HC3 + HO	--> BRO2OHHH	(86)	1.76E+6	-1	0. 1
HC3 + HO	--> HO2	(87)	1.06E+6	-1	0. 1
NO + BRO2OHHH	--> HO2 + MGLY + NO2	(88)	8.80E+7	-1	0. 1
HO + MGLY	--> H2O + RCO3 + CO	(91)	7.04E+6	-1	0. 1
:					
: Reactions of Organic Radicals					
:					
RCO3 + HO2	--> RO2H	(41)	2.64E+6	-1	0. 1
RCO3 + NO	--> RO2 + NO2	(22)	1.13E+6	-1	0. 1
RCO3 + NO2	--> PAN	(23)	5.98E+5	-1	0. 1
PAN	--> NO2 + RCO3	(43)	4.74E+16	0 12516.	1
RO2 + NO	--> RO + NO2	(21)	3.08E+6	-1	0. 1
HO2 + RO2	--> RO2H + O2	(28)	1.19E+6	-1	0. 1
RO2 + RO2	--> 2 RO + O2	(29)	1.76E+5	-1	0. 1
RO2 + O3	--> RO + O2	(38)	4.84E+3	-1	580. 1
RO + O2	--> HO2 + HC4	(24)	2.20E+5	-1	2000. 1
RO + NO2	--> RNO3	(25)	4.40E+6	-1	0. 1
:					
: These terms are the Photolysis reaction steps (J1 - J12)					
:					
NO2 + HV	--> NO + O	(51)	0.30	0	0. 2
O3 + HV	--> O + O2	(58)	1.62E-2	0	0. 2
O3 + HV	--> O2 + 2 HO	(59)	1.37E-4	0	0. 2
HNO2 + HV	--> HO + NO	(52)	6.60E-2	0	0. 2
H2O2 + HV	--> 2 HO	(53)	3.72E-4	0	0. 2
NO3 + HV	--> NO2 + O	(57)	5.70	0	0. 2
NO3 + HV	--> NO + O2	(83)	0.72	0	0. 2
N2O5 + HV	--> 2 NO2 + O	(60)	9.96E-7	0	0. 2
HC4 + HV	--> CO	(42)	4.80E-4	0	0. 2
HC4 + HV	--> CO + 2 HO2	(50)	3.90E-4	0	0. 2
HC4 + HV	--> RO2 + HO2 + CO	(54)	3.90E-4	0	0. 2
MGLY + HV	--> RCO3 + HO2 + CO	(90)	1.38E-2	0	0. 2

TABLE 12 (Continued)

REACTION	NUMBER	RATE CONSTANT ^b			KEY
		A	B	C	
:					
:	Wall loss terms				
:					
	O3 --> WALL	(62)	1.68E-03	0	0. 1
	H2O2 --> WALL	(71)	4.20E-03	0	0. 1
:					

Footnotes for Table 12

- (a) Mechanism Documentation: Gelinas et al. (1974), Luther and Gelinas (1976), Gelinas and Skewes-Cox (1977), MacCracken and Sauter eds. (1975) and Penner and Walton (1982). A computer tape containing the reaction mechanism was obtained from J. Penner, Lawrence Livermore National Laboratory, Livermore, California, on 2 July 1982. There are a number of differences between the mechanism described in Penner and Walton (1982) and Table 12. Several reaction steps have been included to account for wall effects in smog chamber experiments.
- (b) Reaction rate constants are of the form $k = A * TEMP^B * \exp(-C/TEMP)$ with units in terms of the ppm-min system. Note that the values used in this table have been converted from the cgs system reported in Penner and Walton (1982).
- (c) HNO_3 , RNO_2 , RNO_3 , RO_2H , Wall, H_2O , M_0 and O_2 are not calculated in the PW mechanism.

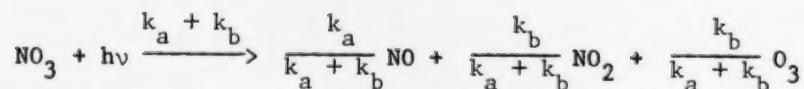
TABLE 13

Species Used in the Penner and Walton (1982) Reaction Mechanism

NUMBER	CODE	I.C. ^a	SPECIES NAME
1	BRO2OHHH		Oxygenated aromatic radical
2	CO	2.50	Carbon monoxide
3	HC1	1.29	Alkenes, isoprene and mono-terpenes
4	HC2	0.78	Alkanes
5	HC3	1.91	Aromatics
6	HC4	0.0143	Aldehydes and ketones
7	HNO2		Nitrous acid
8	HNO3		Nitric acid
9	HNO4		Peroxy nitric acid
10	HO		Hydroxyl radical
11	HO2		Hydroperoxyl radical
12	H2O	21219.	Water vapor
13	H2O2		Hydrogen peroxide
14	M	1000000.	Third body for deactivation
15	MGLY		Methylglyoxal
16	NO	0.744	Nitric Oxide
17	NO2	0.260	Nitrogen Dioxide
18	NO3		Nitrogen trioxide (nitrate radical)
19	N2O5		Dinitrogen pentoxide
20	O		Atomic oxygen
21	O2	210162.	Molecular oxygen
22	O3		Ozone
23	PAN		Peroxyacetyl nitrate
24	RCO3		Peroxyacyl radical
25	RNO2		Alkyl nitrite
26	RNO3		Alkyl nitrate
27	RO		Alkoxy radical
28	RO2		Alkylperoxy radical
29	RO2H		Peroxide
30	WALL		Loss term

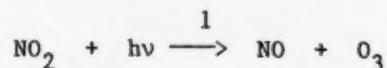
(a) The initial conditions correspond to smog chamber experiment number EC245 carried out at the University of California Riverside. The additional data needed to characterize the experimental conditions are:

Dilution Rate = 0.0003 min^{-1}
 Chamber Temperature = $302.6 \text{ }^{\circ}\text{K}$

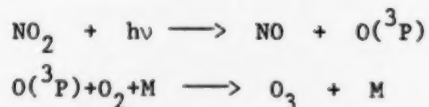


Under typical atmospheric conditions both of the simplifying assumptions are reasonable. The final form used by Atkinson et al. (1982) is based on measurements that give $k_a/(k_a + k_b) \cong 0.3$ and $k_b/(k_a + k_b) \cong 0.7$. The procedure for combining reactions can be used in reverse to eliminate non-integer stoichiometric coefficients.

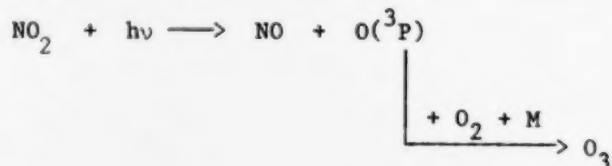
In many cases species can be eliminated from the reaction set if their characteristic reaction times are very short. In some cases this can lead to apparent violations of mass conservation. Consider the first reaction in the Atkinson et al. (1982) mechanism



As in the previous example this reaction is the result of combining two elementary reaction steps

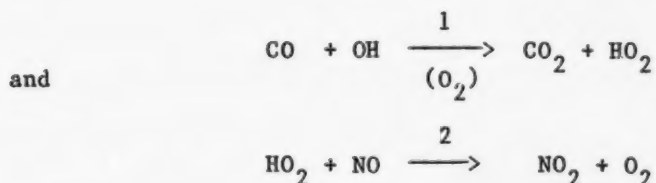


Since the second step is very fast, the two reactions can be written as

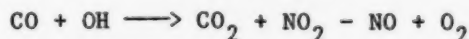


to give the composite form used in the mechanism. The use of this

simplification has reduced the number of reactions and species. In some cases however, the elimination of fast intermediates can lead to the appearance of negative stoichiometric coefficients. To illustrate this point consider the reactions



If the second reaction is considerably faster than the first then HO_2 can be eliminated to give the equivalent step with one negative stoichiometric coefficient



This approach is used in the Atkinson et al. (1982) mechanism to treat NO to NO_2 conversions by the intermediate radicals that are generated as a result of OH attack on organics.

2.2 Numerical Solution of the Chemical Kinetics

There are many computer programs available for the routine solution of chemical kinetics. Operationally these programs accept a description of the reaction mechanism and then use numerical solution techniques to calculate the species concentration dynamics. In this study extensive use has been made of the CHEMKIN package developed by Kee et al. (1980). There were several reasons for selecting this particular approach. Perhaps the most important was that CHEMKIN provided a very general framework for manipulating and solving complex

reaction mechanisms. By using the concept of a chemical compiler (Edelson; 1975, 1976, 1981) it is possible to algebraically manipulate the governing differential equations. This capability simplifies the implementation of sensitivity analysis procedures such as the FAST method (Koda et al. 1979; McRae et al. 1982) or the direct techniques of Kramer et al. (1981, 1982). In addition to CHEMKIN, we have made extensive use of the program CHEMK developed by Whitten and Hogo (1980). For further details about these and other analysis programs the reader is referred to McRae (1983).

2.3 Implementation and Initial Mechanism Testing

Before subjecting any mechanism to a detailed evaluation it is important to ensure that the reaction scheme has been implemented in the manner intended by each investigator. Four basic tests were carried out: duplication of the sample calculations supplied by each investigator, a check on mass conservation properties, modeling of a particular smog chamber experiment and finally the preparation of a standard isopleth. Full details of each test have been compiled in a form suitable for distribution to the investigators who have submitted mechanisms for evaluation. In the interests of space the results of these tests are not presented here.

All of the mechanisms considered in this study were supplied with a test problem. The first step in verifying that the mechanism had been implemented correctly was to reproduce the results of the test problem. Given the initial conditions and the reaction stoichiometry shown in Tables 2-13 each mechanism was used to predict the

concentration time histories. In all cases the sample problems were reproduced to within acceptable accuracy.

CHAPTER 3

DISCUSSION OF THE CHEMICAL FORMULATION OF THE MECHANISMS

3.1 Carbonyl Chemistry and Lumping

The treatment of carbonyl chemistry in each of the lumped mechanisms is summarized in Table 14. For reference, the photooxidation mechanisms of formaldehyde, acetaldehyde, and propionaldehyde and of acetone and methyl ethyl ketone are given in Figures 2 and 3, respectively.

In the ALW mechanism, aldehydes are represented by HCHO , CH_3CHO and RCHO , where the reactions of RCHO are those of propionaldehyde. Thus the first three aldehydes serve as surrogates for all aldehydes; specifically propionaldehyde serves as a surrogate for itself and all higher aldehydes. Acetone and methyl ethyl ketone are treated explicitly. The only acetone reaction included is photolysis, whereas both photolysis and OH-reaction are included for methyl ethyl ketone. The methyl ethyl ketone-OH reaction is assumed to proceed totally by the path resulting from internal carbon atom OH attack. Because of the relative slowness of the OH reaction, this assumption is not expected to be a source of error.

The photolysis products in the Demerjian mechanism are consistent with the assumption that the generalized aldehyde species HC_3 consists of a 50/50 mixture of formaldehyde and higher aldehydes, whereas the products of the $\text{HC}_3\text{-OH}$ reaction reflect an assumed distribution of 70 percent formaldehyde and 30 percent higher aldehydes. In the PW

TABLE 14
Representation of Carbonyl Chemistry by Lumped Mechanisms

MECHANISM	REACTIONS ^a	COMMENTS
Atkinson et al. (1982) (ALW)	See Table 2	Explicit chemistry of HCHO, CH ₃ CHO, CH ₃ CH ₂ CHO, CH ₃ C(O)CH ₃ and CH ₃ CH ₂ C(O)CH ₃
Demerjian (1982)	$\text{HC3} + h\nu \longrightarrow 0.5 \text{ RO}_2 + 1.5 \text{ HO}_2 + \text{CO}$ $\text{HC3} + \text{OH} \longrightarrow 0.3 \text{ RHO}_2 + 0.7 \text{ HO}_2$ $+ 0.7 \text{ CO}$	Generalized aldehyde species HC3
McRae and Seinfeld (1983) (MS)	HCHO explicit $\text{RCHO} + h\nu \longrightarrow \text{RO}_2 + \text{HO}_2 + \text{CO}$ $\text{RCHO} + \text{OH} \longrightarrow \text{RCO}_3$	Aldehydes divided into HCHO and higher aldehyde RCHO with CH ₃ CHO rate constants
Killus and Whitten (1982) (KW)	$\text{CARB} + h\nu \longrightarrow \text{H}_2 + \text{CO}$ $\longrightarrow (1-a)\text{HO}_2 + (1-a)\text{MEO}_2$ $+ \text{CO} - (1-a)\text{PAR}$ $\text{CARB} + \text{OH} \longrightarrow \text{HO}_2 + \text{CO}_2 + \text{H}_2\text{O} \quad (52\%)$ $\longrightarrow \text{ACO}_3 + \text{H}_2\text{O} - \text{PAR} \quad (44\%)$ $\longrightarrow \text{CRO}_2 - \text{PAR} \quad (4\%)$	See text
Penner and Walton (1982) (PW)	$\text{HC4} + h\nu \longrightarrow \text{CO} \quad (38\%)$ $\longrightarrow \text{CO} + 2\text{HO}_2 \quad (31\%)$ $\longrightarrow \text{RO}_2 + \text{HO}_2 + \text{CO} \quad (31\%)$ $\text{HC4} + \text{OH} \longrightarrow \text{RCO}_3 + \text{H}_2\text{O} \quad (63\%)$ $\longrightarrow \text{CO} + \text{HO}_2 + \text{H}_2\text{O} \quad (37\%)$	Generalized aldehyde species HC4

Footnotes for Table 14:

- ^a When we write reactions from these mechanisms we will use the species nomenclature employed by the mechanism developers. Thus, even though each of these three mechanisms employs the generalized species, RO_2 , this species has a specific definition in each mechanism. In all cases, RO_2 , is a peroxy radical, although its reactions are somewhat different in each of the three mechanisms.

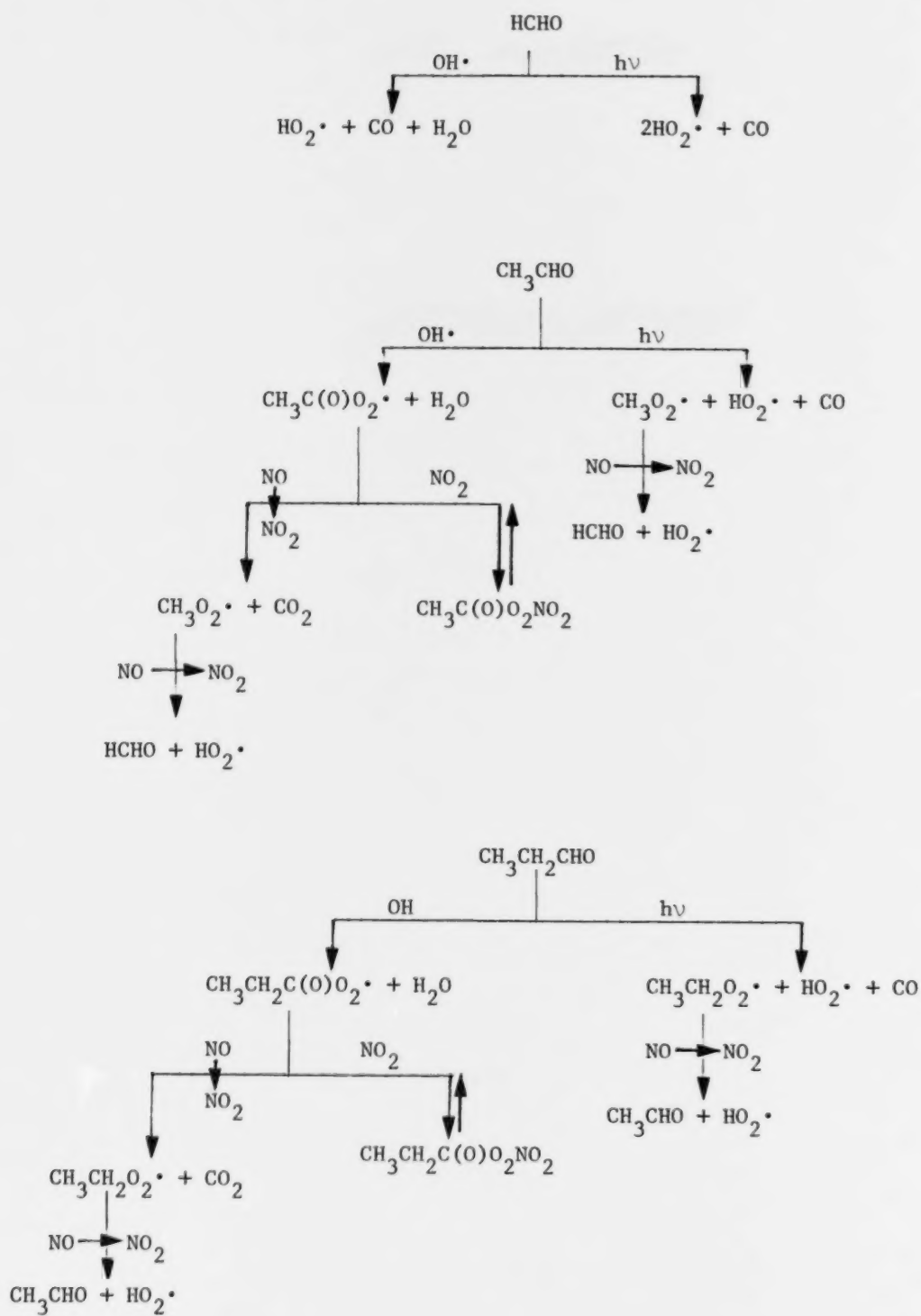


Figure 2. Formaldehyde, Acetaldehyde and Propionaldehyde Photooxidation Mechanisms

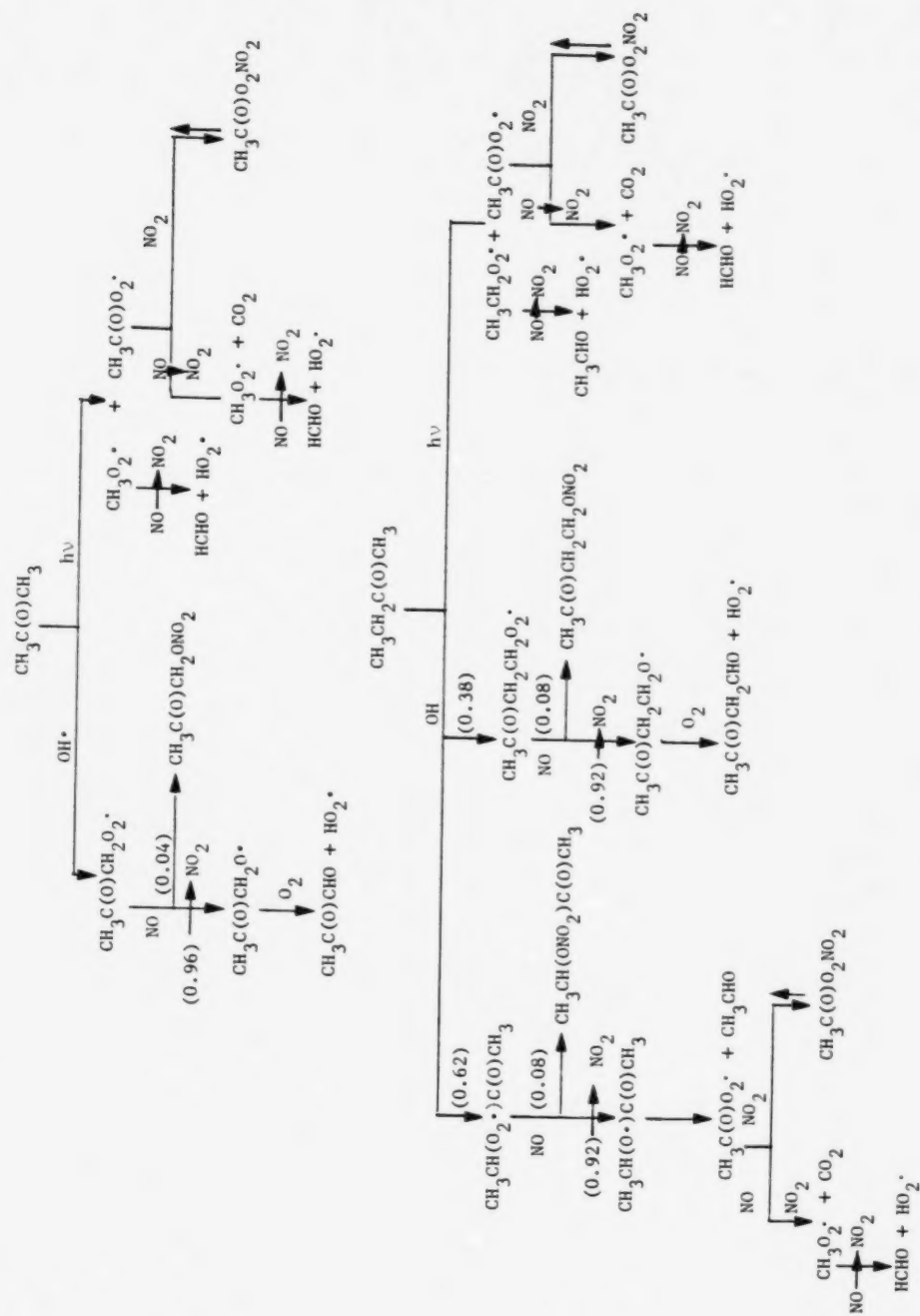


Figure 3. Acetone and Methyl Ethyl Ketone Photooxidation Mechanisms

mechanism, the lumped group HC4 is treated as 0.5 HCHO and 0.5 CH₃CHO. Thus, the three photolysis steps of HC4 are assigned rates equal to one-half those for HCHO and CH₃CHO. The KW mechanism requires some development to understand how its carbonyl chemistry was arrived at, and thus we now discuss that mechanism.

The KW mechanism, referred to as the Carbon Bond mechanism, represents carbonyl species as a combination of the two lumped species, CARB and PAR, where [CARB] is the total concentration of carbonyl groups and [PAR] is the sum of the number of carbon atoms in each alkane group,

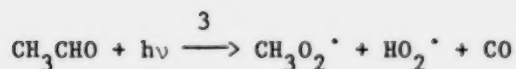
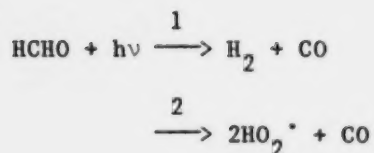
$$[\text{PAR}] = \sum_i n_i [\text{RH}_i] + \sum_i m_i [\text{CX}_i]$$

where n_i is the number of carbon atoms in alkane RH_i and m_i is the number of paraffinic carbon atoms in other types of molecules, CX_i , e.g. carbonyl compounds. For a four aldehyde system, for example,

$$[\text{CARB}] = [\text{HCHO}] + [\text{CH}_3\text{CHO}] + [\text{CH}_3\text{CH}_2\text{CHO}] + [\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}]$$

$$[\text{PAR}] = [\text{CH}_3\text{CHO}] + 2[\text{CH}_3\text{CH}_2\text{CHO}] + 3[\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}]$$

To develop the treatment of aldehyde chemistry in the KW mechanism, let us consider first the photolysis of formaldehyde and acetaldehyde,



If $[\text{CARB}] = [\text{HCHO}] + [\text{CH}_3\text{CHO}]$, then the decay of $[\text{CARB}]$ due to photolysis is described by

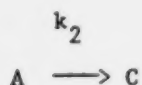
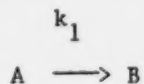
$$-\frac{d[\text{CARB}]}{dt} = k_1[\text{HCHO}] + k_2[\text{HCHO}] + k_3[\text{CH}_3\text{CHO}] \quad (3.1)$$

Letting $a = [\text{HCHO}]/[\text{CARB}]$, this relation becomes

$$-\frac{d[\text{CARB}]}{dt} = ak_1[\text{CARB}] + \{ak_2 + (1-a)k_3\}[\text{CARB}] \quad (3.2)$$

Based on (3.2), the photolysis of CARB can be expressed as three parallel reactions,*

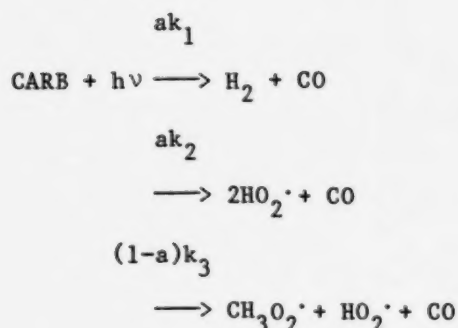
* Consider the two parallel first-order reactions



Then

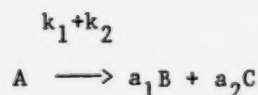
$$\frac{d[\text{A}]}{dt} = -(k_1 + k_2)[\text{A}]$$

$$\frac{d[\text{B}]}{dt} = k_1[\text{A}] \quad \text{and} \quad \frac{d[\text{C}]}{dt} = k_2[\text{A}]$$



Actually it is desired to represent these three reactions as two, an inert product path (reaction 1) and a radical producing path (reactions

We can express the two parallel reactions as a single reaction



that has the overall first-order rate constant k_1+k_2 . The rate of formation of B is given by a_1 times the rate of the reaction,

$$\frac{d[\text{B}]}{dt} = a_1(k_1 + k_2)[\text{A}]$$

Likewise,

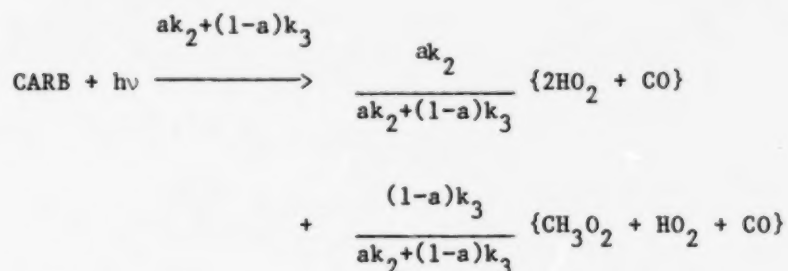
$$\frac{d[\text{C}]}{dt} = a_2(k_1 + k_2)[\text{A}]$$

For these rates to equal those of the original parallel reactions,

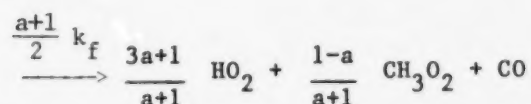
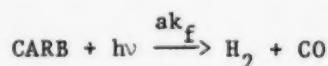
$$a_1 = \frac{k_1}{k_1 + k_2} \qquad a_2 = \frac{k_2}{k_1 + k_2}$$

Thus, a_1 is just the fraction of the overall rate constant, $k_1 + k_2$, for reaction 1, and likewise for a_2 . In other words, if A decays with a total rate $k_1 + k_2$, the fraction of that rate ascribable to reaction 1 is the fraction of products that is B. In this manner, parallel reactions can be combined into a single overall reaction.

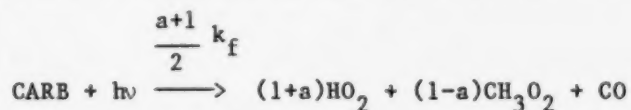
2 and 3). Writing the second and third reactions as a single reaction, we obtain the radical-producing path as



In the KW mechanism the rate constants k_1 , k_2 and k_3 are related by $k_1 = k_2 = 2k_3 = k_f$. With this relation among the three rate constants, the correct representation of the two CARB photolysis steps is



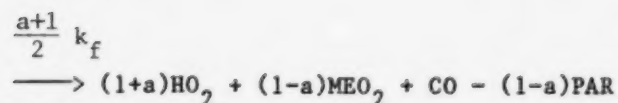
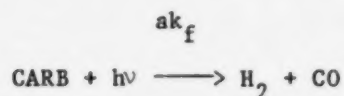
However, in the KW mechanism the second reaction is written as



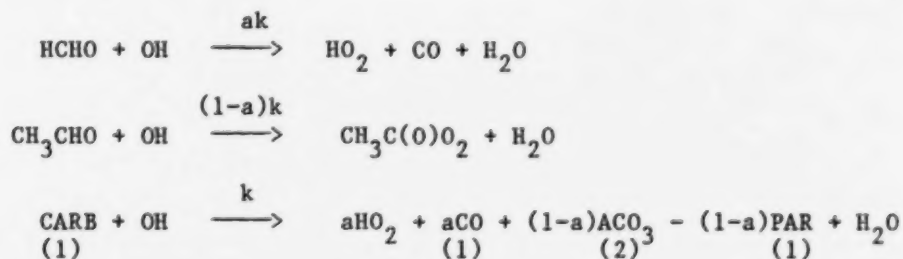
In this form the rate constants and stoichiometric coefficients are inconsistent. In the KW mechanism, however, CARB represents species other than HCHO and CH₃CHO. It is therefore difficult to assess theoretically the impact of this choice of coefficients.

As we will see shortly, instead of CH₃O₂, the KW mechanism uses the generalized species MEO₂ that contains one carbon atom. Thus, the

CARB photolysis reactions are written as,

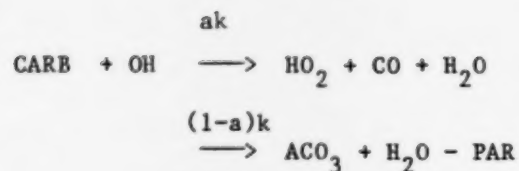


The $(1-a)\text{PAR}$ term must be subtracted to transfer the needed carbon atom for MEO_2 from the PAR pool to the MEO_2 pool.* In the KW mechanism, the parameter a actually represents $([\text{HCHO}] + [\text{KETONES}])/[\text{CARB}]$. This definition does not change the stoichiometric coefficient error noted above, however. The general CARB-OH reaction can be developed from HCHO and CH_3CHO :



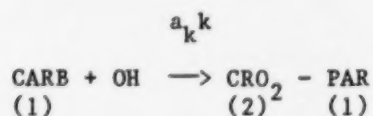
where the number in parenthesis below a species indicates the number of carbon atoms in the species. This reaction can be written as $(\text{ACO}_3$ is the KW designation for $\text{CH}_3\text{C(O)O}_2$)

* The transfer can also be effected by replacing $-(1-a)\text{PAR}$ with $(1-a)\text{X}$, followed by the rapid reaction $\text{X} + \text{PAR} \longrightarrow$. This device is what is actually employed in the KW mechanism.

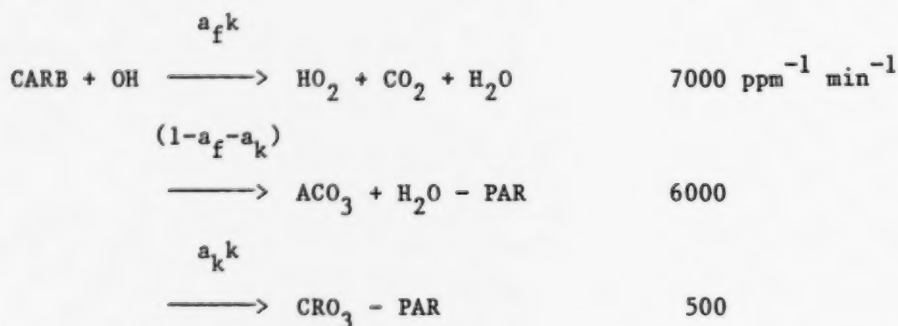


where k is an average rate constant for all carbonyl-OH reactions.

If the group CARB includes ketones in addition to aldehydes, the following reaction is added



where CRO_2 denotes the peroxy radical formed from OH attack on a ketone. The composite mechanism can now be written in the form, where we include the rate constants to show the assumed split among the three steps,



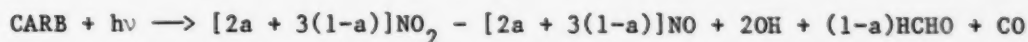
In the KW mechanism ketone chemistry is represented through the OH reaction of the fraction of CARB assumed to be ketones. While accomplishing an economy of species, the lumping of aldehydes and ketones together in the CARB species neglects differences in the photolysis rates and OH mechanisms of the two classes of compounds. The ketone-OH reaction generally proceeds by attack on a hydrogen atom adjacent to the carbonyl group, followed by elimination of an aldehyde

and an acylperoxy radical, including an NO/NO_2 conversion. The competitive rates of photolysis and OH attack are different between aldehydes and ketones. The attempt to represent this difference is reflected by the percentage of CARB-OH reactions that proceed to give CRO_2 . This split is fixed in the KW mechanism and thus does not reflect the actual distribution of aldehydes and ketones comprising CARB in a particular application.

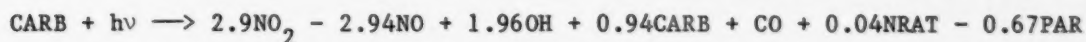
Let us summarize the results of this section. By considering the treatment of carbonyl chemistry in each of the five mechanisms, we have provided examples of the lumping approaches delineated in Figure 1. In the surrogate species lumped molecule approach of the ALW mechanism, the representation of carbonyl chemistry is exact through propionaldehyde and methyl ethyl ketone, and higher aldehydes and ketones are represented by a comparable concentration of propionaldehyde and methyl ethyl ketone. The three generalized species lumped molecule mechanisms require one to partition all aldehydes into one or two lumped classes.

All carbonyl compounds are represented by the single species CARB in the KW mechanism, the concentration of which is equal to that of all -C=O groups. In deriving the photolysis and OH reactions of the CARB species, a formaldehyde/higher aldehyde split is implicit in the choice of rate constants and stoichiometric coefficients.

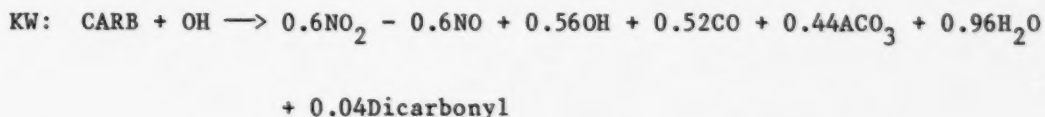
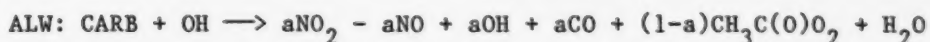
We can compare the ALW and KW aldehyde reactions. If we let a be the formaldehyde fraction of total aldehydes, then the ALW aldehyde reaction can be written as



whereas the KW step is



The aldehyde-OH steps are:



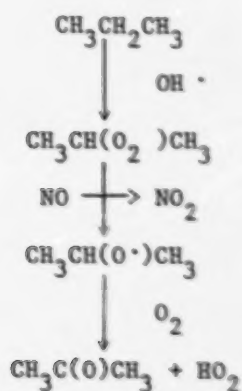
A value of $a \approx 0.1$ in the ALW mechanism produces comparable stoichiometries in the carbonyl photolysis steps of the two mechanisms, whereas a value of $a \approx 0.6$ is needed for the two carbonyl-OH steps to correspond.

3.2 Alkane Photooxidation Chemistry

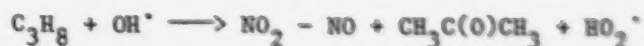
We now consider the atmospheric chemistry of alkanes. Since OH reaction is the only significant alkane oxidation process in the atmosphere, we consider only that reaction here. The general features of

the alkane-OH reaction are, first, OH abstraction of a hydrogen atom from a terminal or internal carbon atom, followed by rapid addition of O_2 to form a peroxyalkyl radical, the principal fate of which is reaction with NO to give either NO_2 and an alkoxy radical or an alkyl nitrate. The key issues in alkane photooxidation chemistry are 1) the relative proportions of alkoxy radical and NO_2 formation versus alkyl nitrate formation in the peroxyalkyl-NO reaction, and 2) the fate of the alkoxy radical produced in the peroxyalkyl-NO reaction.

To elucidate the representation of alkane chemistry in the lumped mechanisms we will consider the explicit chemistry of propane, n-butane, and 2,3-dimethylbutane. The propane-OH photooxidation mechanism is:



Internal H-atom abstraction predominates, and alkyl nitrate formation does not occur in the $\text{CH}_3\text{CH}(\text{O}_2^\cdot)\text{CH}_3$ -NO reaction. The overall reaction can be written as:



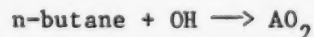
The n-butane-OH reaction leads to the mechanism given in Figure 4. Definitive data concerning the relative importance of the two paths of reaction of the sec-butoxy radical, $\text{CH}_3\text{CH}_2\text{CH}(\text{O}^\bullet)\text{CH}_3$, are not currently available, and Atkinson and Lloyd (1983) do not recommend a firm value for the ratio of the rate constants of these two reactions. Consequently, the split is indicated by the fraction b in the n-butane mechanism.

Finally, we consider the photooxidation of 2,3-dimethylbutane, as given in Figure 5.

We now consider the representation of alkane chemistry by the lumped mechanisms as given in Table 15. The propane, n-butane and 2,3-dimethylbutane photooxidation mechanisms provide a benchmark to evaluate the lumped alkane steps.

SURROGATE SPECIES LUMPED MOLECULE MECHANISM (ALW)

The ALW mechanism represents alkane chemistry through the explicit chemistries of propane, n-butane, and $\geq \text{C}_4$ alkanes. The n-butane reaction given in Table 15 can be derived as follows. The first step is written as



where AO_2 consists of 0.85 of 2-butyl peroxy and 0.15 of 1-butyl peroxy. Based on the splits in the n-butane mechanism above, the reaction of AO_2 and NO is written as (assuming $b = 0.38$),

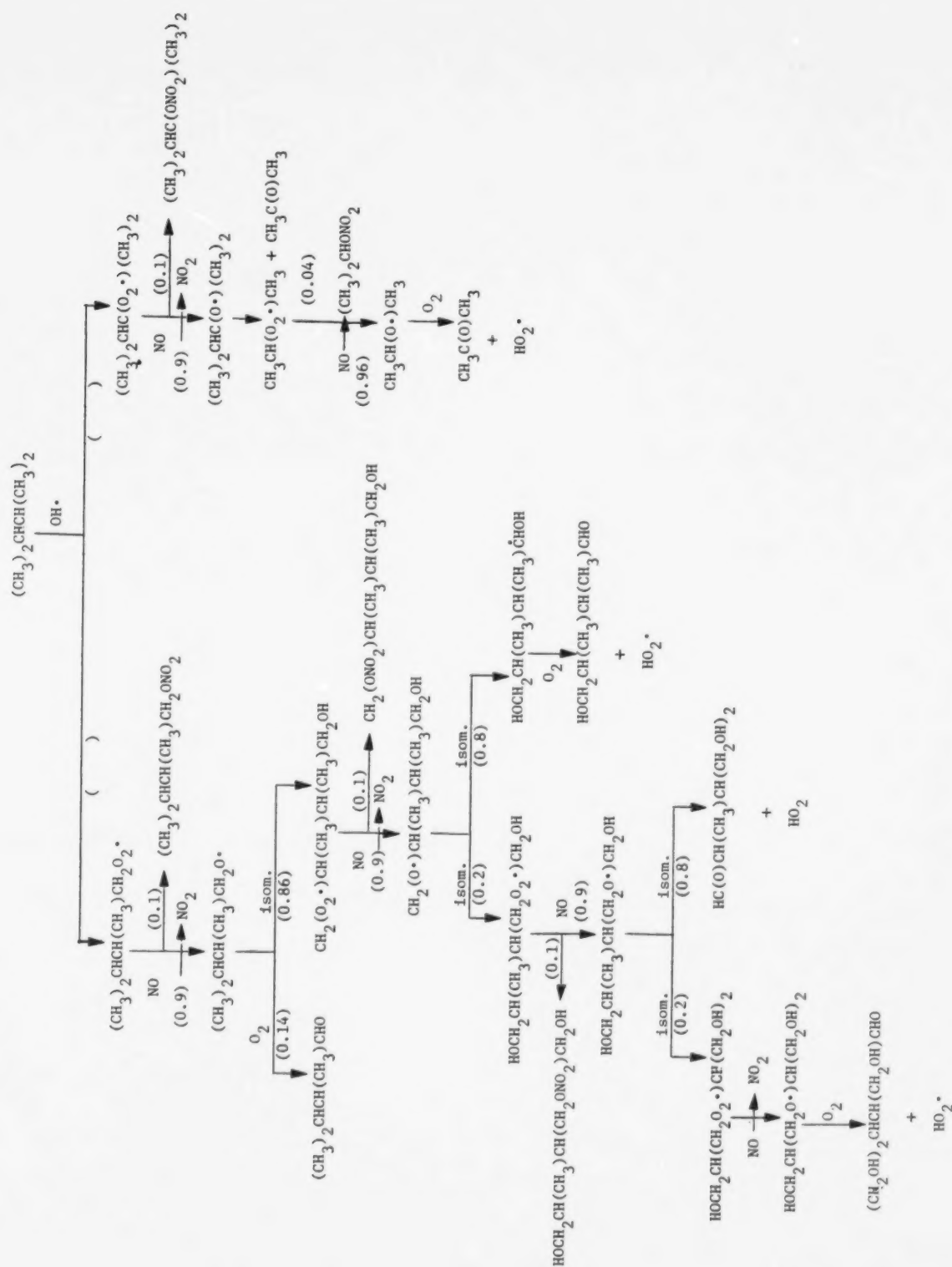


Figure 5. 2,3-Dimethyl butane Photooxidation Mechanism

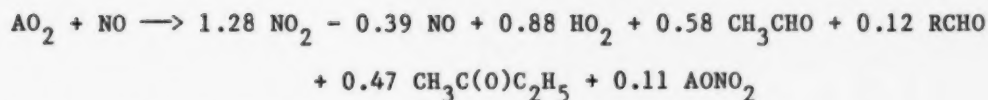
TABLE 15

Representation of Alkane Chemistry by Lumped Mechanisms

MECHANISM	REACTIONS	COMMENTS
Atkinson et al. (1982) (ALW)	$C_3H_8 + OH \longrightarrow NO_2 + NO + CH_3C(O)CH_3 + HO_2$ $n\text{-butane} + OH \longrightarrow AO_2$ $AO_2 + NO \longrightarrow 1.28 NO_2 - 0.39 NO + 0.88 HO_2 + 0.58 CH_3CHO$ $+ 0.12 RCHO + 0.47 CH_3C(O)C_2H_5 + 0.11 AONO_2$ $C_4 \text{ alkanes} + OH \longrightarrow BO_2$ $BO_2 + NO \longrightarrow 1.7 NO_2 - 0.8 NO + 0.9 HO_2 + 0.15 HCHO + 0.3 CH_3CHO$ $+ 0.1 RCHO + 0.3 CH_3C(O)CH_3 + 0.45 CH_3C(O)C_2H_5$ $+ 0.11 AONO_2$	Propane, n-butane and $\geq C_4$ alkanes
Demerjian (1982)	$HC2 + OH \longrightarrow RO_2$ $RO_2 + NO \longrightarrow NO_2 + RO$ $RO + O_2 \longrightarrow HC3 + HO_2$	Generalized alkane species HC2, peroxyalkyl radical RO_2 , and alkoxy radical RO
McRae and Seinfeld (1983) (MS)	$ALK + OH \longrightarrow RO_2$ $RO_2 + NO \longrightarrow NO_2 + RO$ $RO \longrightarrow b_1HO_2 + b_2HCHO + b_3RCHO + b_4RO_2$	Generalized alkane species ALK peroxy radical RO_2 , and alkoxy radical RO
Killus and Whitten (1982) (KW)	$PAR + OH \longrightarrow MEO_2 + H_2O$ $MEO_2 + NO \longrightarrow NO_2 + CARB + HO_2 \quad (64\%)$ $\longrightarrow NO_2 + CARB + MEO_2 - PAR \quad (32\%)$ $\longrightarrow NRAT \quad (4\%)$	PAR represents single- bonded carbon atoms

TABLE 15 (continued)

MECHANISM	REACTIONS	COMMENTS
Penner and Walton (1982) (PW)	$\text{HC2} + \text{OH} \longrightarrow \text{RO}_2 + \text{H}_2\text{O}$	Generalized alkane species HC2, peroxyalky radical RO_2 , and alkoxy radical RO
	$\text{RO}_2 + \text{NO} \longrightarrow \text{NO}_2 + \text{RO}$	
	$\text{RO} + \text{O}_2 \longrightarrow \text{HC4} + \text{HO}_2$	



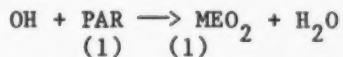
with a similar approach to deriving the $\geq \text{C}_4$ -alkane-OH reaction.

3.2.1 Generalized Species Lumped Molecule Mechanisms

The generalized alkane-OH reactions of the Demerjian, MS and PW mechanisms given in Table 15 are self-explanatory except for the generalized alkoxy radical reaction in the MS mechanism. We defer discussion of that step until we consider alkene chemistry since the generalized alkoxy radical in the MS mechanism arises from both alkane and alkene reactions.

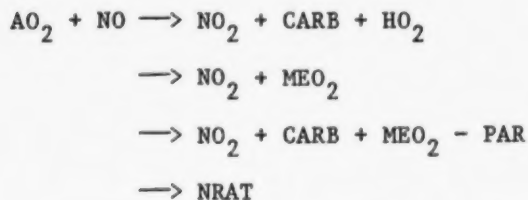
3.2.2 Carbon Bond Mechanism (KW)

Let us now consider the KW mechanism and the carbon bond lumping approach to alkane-OH chemistry. The first step is

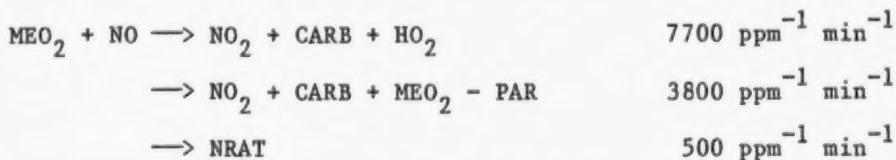


Because alkane carbon atoms are represented by the single species PAR, it is necessary to assign a rate constant for this reaction that is, in some sense, an average OH-rate constant for all reactions represented by the single PAR-OH reaction. Based on alkane-OH rate constants and on the composition of typical atmospheric mixtures, KW chose a rate constant of $1300 \text{ ppm}^{-1} \text{ min}^{-1}$, slightly less than the value for a secondary carbon atom.

By considering the n-butane-OH mechanism and letting $[AO_2] = [CH_3CH_2CH(O_2^{\cdot})CH_3] + [CH_3CH_2CH_2CH_2O_2^{\cdot}]$, the AO_2 -NO reaction can be expressed in Carbon Bond nomenclature as



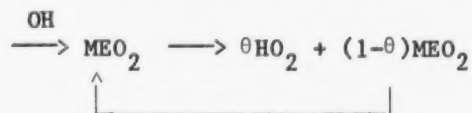
Because the general peroxyalkyl radical MEO_2 arises from aldehydes, aromatics, etc. in addition to alkanes, the above reactions with MEO_2 replacing AO_2 are too specific to the alkane system to represent the general MEO_2 -NO reaction. The general MEO_2 -NO reaction adopted in the KW mechanism, together with the rate constants used, is



If the total $\text{MEO}_2\text{-NO}$ rate constant $k = 12000 \text{ ppm}^{-1} \text{ min}^{-1}$ is apportioned according to

$$\begin{aligned}\theta v_k &= 7700 \\ (1-\theta)v_k &= 3800 \\ (1-\psi)k &= 500\end{aligned}$$

where ν is the fraction of $\text{MEO}_2\text{-NO}$ reactions that leads to NO_2 , i.e. 0.96, then θ can be interpreted in terms of the following cycle

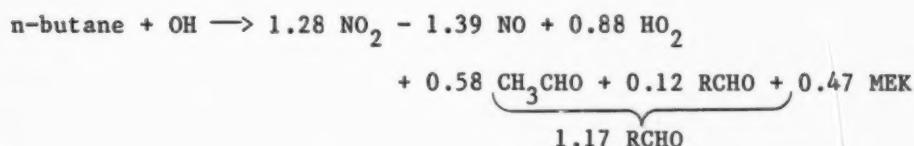


Thus, the total number T of MEO_2 molecules produced from one molecule of MEO_2 is

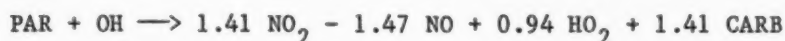
$$T = \sum_{n=1}^{\infty} (1-\theta)^{n-1} = \frac{1}{\theta}$$

In the KW mechanism, the values of the rate constants used imply that $\theta = 0.67$ or $T = 1.5$.

The ALW n-butane-OH reaction may be written as



Whereas the comparable step in the KW mechanism is



Thus, the KW mechanism is slightly more reactive than the ALW mechanism in terms of this step.

3.3 Alkene Photooxidation Chemistry

3.3.1 Alkene-O and Alkene-OH Reactions

Alkene-O and alkene-OH reactions in the lumped mechanisms are given in Tables 16 and 17, respectively. For comparison, the detailed chemistry of ethene, propene, and trans-2-butene is given in Figures 6 and 7. Since alkene-O atom reactions are not of major importance in photochemical smog, their omission is not expected to be a source of error.

TABLE 16

Alkene-O Reactions in the Lumped Mechanisms

MECHANISM	REACTIONS	COMMENTS
Atkinson et al. (1982) (ALW)		Not included
Demerjian (1982)	$\text{HCl} + \text{O} \longrightarrow \text{RO}_2 + \text{HC}_3 + \text{HO}_2$	
Killus and Whitten (1982a) (KW)	$\text{OLE} + \text{O} \longrightarrow \text{MEO}_2 + \text{ACO}_3 + \text{X}$ $\longrightarrow \text{CARB} + \text{PAR}$ $\text{ETH} + \text{O} \longrightarrow \text{MEO}_2 + \text{HO}_2 + \text{CO}$ $\longrightarrow \text{CARB} + \text{PAR}$	
McRae and Seinfeld (1983) (MS)	$\text{C}_2\text{H}_4 + \text{O} \longrightarrow \text{RO}_2 + \text{HO}_2$ $\text{OLE} + \text{O} \longrightarrow \text{RO}_2 + \text{RCO}_3$	
Penner and Walton (1982) (PW)	$\text{HCl} + \text{O} \longrightarrow \text{RO}_2 + \text{RCO}_3$	

TABLE 17

Alkene-OH Reactions in the Lumped Mechanisms

MECHANISM	REACTION	COMMENTS
Atkinson et al. (1982) (ALW)	$C_2H_4 + OH \longrightarrow NO_2 - NO + 2HCHO + HO_2$	Ethene, propene, and trans-2-butene
	$C_3H_6 + OH \longrightarrow NO_2 - NO + CH_3CHO$ $+ HCHO + HO_2$	
	$C_4H_8 + OH \longrightarrow 0.9 NO_2 - NO + 1.8 CH_3CHO$ $+ 0.9 HO_2 + 0.1 RONO_2$	
Demerjian (1982)	$HCl + OH \longrightarrow RO_2 + HC3$	Generalized alkene species HCl
	$RO_2 + NO \longrightarrow RO + NO_2$	
	$RO + O_2 \longrightarrow HC3 + HO_2$	
McRae and Seinfeld (1983) (MS)	$OLE + OH \longrightarrow RO_2$	Generalized alkene species OLE
	$RO_2 + NO \longrightarrow RO + NO_2$	
	$RO \longrightarrow b_1 HO_2 + (1-b_1) RO_2 + b_2 HCHO$ $+ b_3 RCHO$	
Killus and Whitten (1982) (KW)	$ETH + OH \longrightarrow RBO_2$	
	$RBO_2 + NO \longrightarrow NO_2 + 2CARB + HO_2$	
	$OLE + OH \longrightarrow RAO_2$	
	$RAO_2 + NO \longrightarrow NO_2 + 2CARB + HO_2$	
Penner and Walton (1982) (PW)	$HCl + OH \longrightarrow RO_2 + HC4$	
	$RO_2 + NO \longrightarrow RO + NO_2$	
	$RO + O_2 \longrightarrow HC4 + HO_2$	

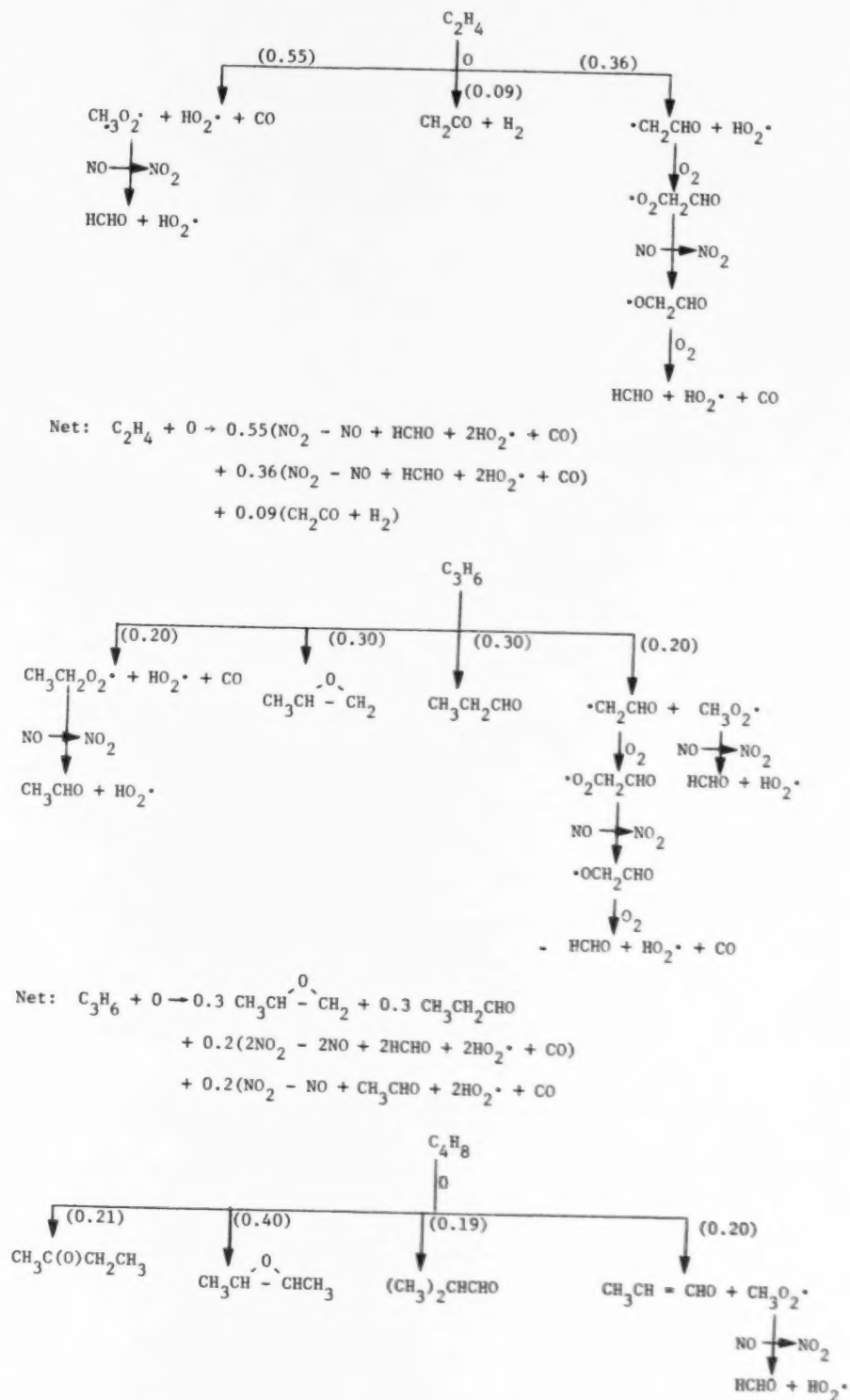


Figure 6. Ethene, Propene, Trans-2-Butene-O Reaction Mechanisms

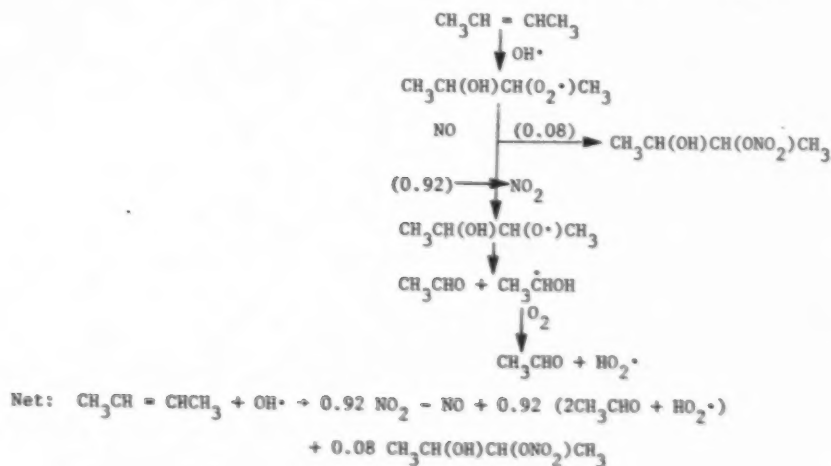
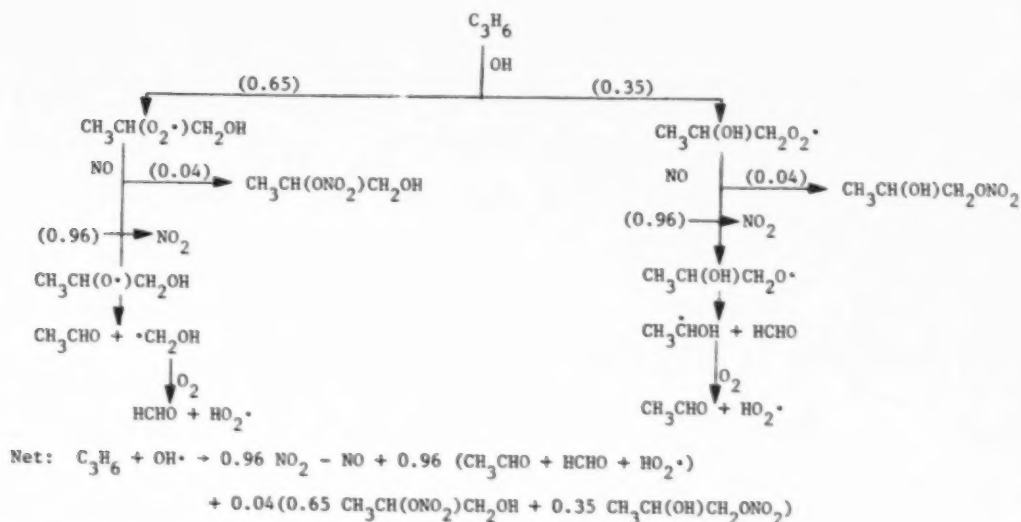
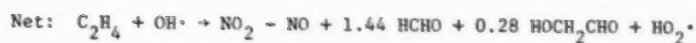
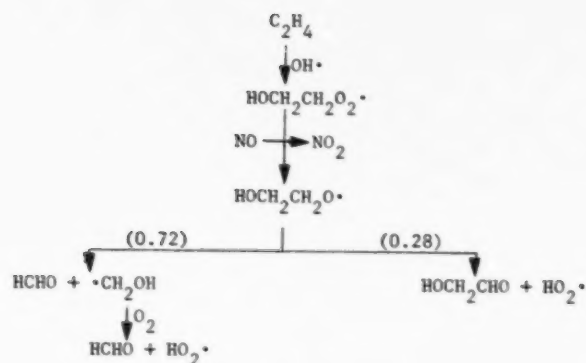


Figure 7. Ethene, Propene, and Trans-2-butene-OH Reaction Mechanisms

Table 17 presents the generalized alkene-OH reactions in the mechanisms. Ethene, propene, and trans-2-butene are treated explicitly in the ALW mechanism. The error incurred by omitting the glycol aldehyde production path in the ethene-OH reaction is not significant since it is implicitly replaced by two formaldehyde molecules. Likewise, the omission of the four percent nitrate forming path in the propene-OH reaction is not expected to be a noticeable source of error. To assess the lumped reaction steps in Table 17, let us review the reactions of several of the alkoxy radicals, as done in Table 18. Most of the alkoxy radical reactions lead to HO_2 , thus HO_2 is a product in each of the RO reactions in each of the three generalized species mechanisms. The Demerjian and PW mechanisms lump all aldehydes into the species HC3 and HC4, respectively, so no distinction need be made between formaldehyde and higher aldehydes in these two mechanisms. Since in the MS mechanism formaldehyde and higher aldehydes are segmented, it is necessary to specify the split of aldehyde products, and values of $b_2 = 0.5$ and $b_3 = 0.5$ have been used. We note that the extra aldehyde produced in the alkene-OH reaction is not included in the MS mechanism as in the other two generalized species mechanisms. Although alkoxy radicals are not treated explicitly in the ALW and KW mechanisms, their assumed chemistry is implicit in the products of the peroxy radical-NO reaction. In the KW mechanism, for example, the implied alkoxy radical chemistry is

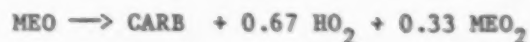
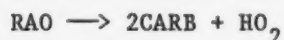


TABLE 18

Alkoxy and Hydroxy Alkoxy Radical Reactions Interpreted According
to $RO \longrightarrow b_1HO_2^{\cdot} + (1-b_1)RO_2^{\cdot} + b_2HCHO + b_3RCHO$

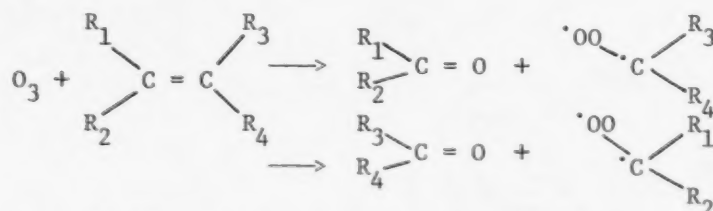
HYDROCARBON SOURCE	RADICAL	b_1	b_2	b_3
Acetaldehyde	$CH_3O^{\cdot}$	1	1	0
Propane	$CH_3CH(O^{\cdot})CH_3$	1	0	1
n-Butane	$CH_3CH_2CH(O^{\cdot})CH_3$	0.62	0	1
	$CH_3CH_2CH_2CH_2O^{\cdot}$	0.25	0	0.25
2,3-Dimethyl butane	$(CH_3)_2CHCH(CH_3)CH_2O^{\cdot}$	0.14	0	0.14
	$(CH_3)_2CHC(O^{\cdot})(CH_3)_2$	0	0	1
Ethene	$HOCH_2CH_2O^{\cdot}$	1	1.44	0.28
Propene	$CH_3CH(O^{\cdot})CH_2OH$	1	1	1
	$CH_3CH(OH)CH_2O^{\cdot}$	1	1	1
trans-2-Butene	$CH_3CH(OH)CH(O^{\cdot})CH_3$	1	0	2



Because the reaction product split from MEO includes 0.33 MEO₂, all else being equal, the KW mechanism can be expected to predict somewhat more reactivity than the other mechanisms that assume 100 percent HO₂ as product.

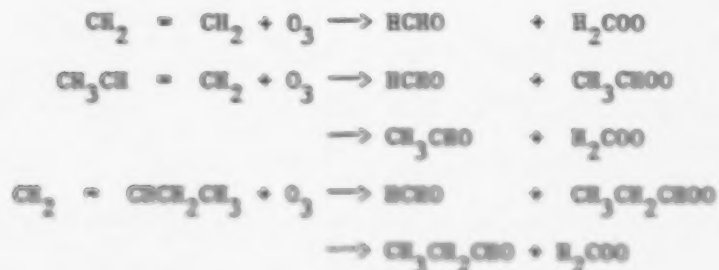
3.3.2 Alkene-O₃ Reactions

It is now reasonably well established that the initial step in the alkene-O₃ reaction is the formation of a molozonide that rapidly decomposes to a carbonyl and an energy-rich biradical, called the Criegee intermediate,



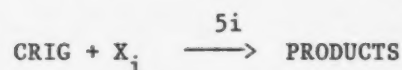
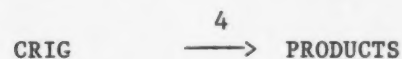
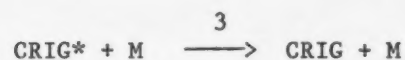
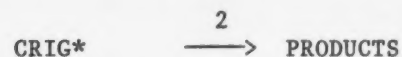
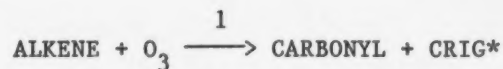
where a 50-50 split between the two paths is usually assumed. The major problem in describing the O₃-alkene reaction lies in establishing the subsequent chemistry of the Criegee intermediate.

The initial O₃ reaction steps for ethene, propene, 1-butene and trans-2-butene are





The dynamics of the Criegee intermediate can be analyzed from the general mechanism:



where CRIG* denotes an energetic form of the Criegee intermediate. If we assume that CRIG* is in a pseudo-steady state, then

$$[\text{CRIG}^*]_{ss} = \frac{k_1[\text{ALKENE}][\text{O}_3]}{k_2 + k_3[\text{M}]}$$

Thus, the kinetics of the stabilized Criegee intermediate CRIG are given by

$$\frac{d[\text{CRIG}]}{dt} = \frac{k_1[\text{ALKENE}][\text{O}_3]}{1 + \frac{k_2}{k_3[\text{M}]}} - \{k_4 + \sum_i k_{5i}[\text{X}_i]\} [\text{CRIG}]$$

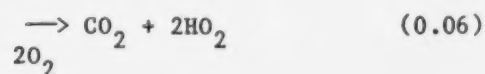
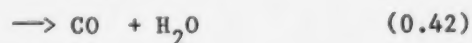
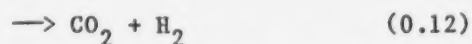
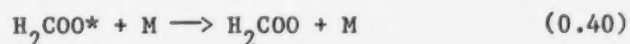
and if CRIG is in a pseudo-steady state,

$$[\text{CRIG}]_{ss} = \frac{k_1[\text{ALKENE}][\text{O}_3]}{\left(1 + \frac{k_2}{k_3[\text{M}]}\right) (k_4 + \sum_i k_{5i}[\text{X}_i])}$$

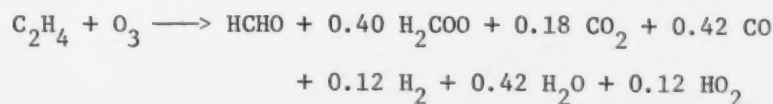
The mechanism above includes two decomposition steps, 2 and 4. If

decomposition occurs, it probably does so via reaction 2, so we can assume that $k_4 = 0$. The ratio $k_3[M]/(k_2 + k_3[M])$ is the fraction of the energetic intermediates that are stabilized.

In their review of the chemistry of H_2COO , Atkinson and Lloyd (1983) recommend the following fate of H_2COO ,

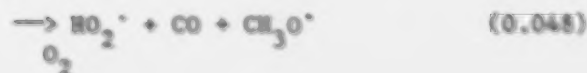
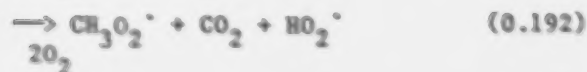
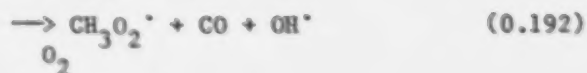
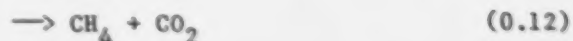
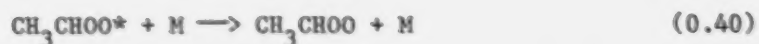


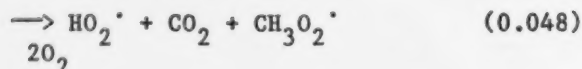
The ethene- O_3 reaction can then be written as



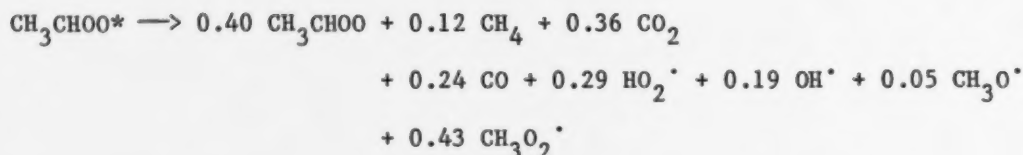
The thermalized H_2COO biradicals can react with CO , $HCHO$, CH_3CHO , NO_x , SO_2 and H_2O . The rates of reaction of the biradicals with these species, however, are unknown.

For the chemistry of the CH_3CHOO biradical, Atkinson and Lloyd (1983) recommend

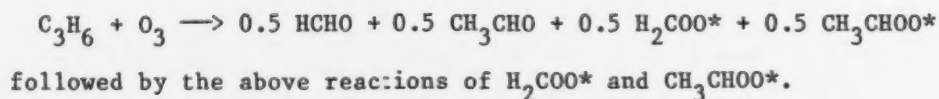




leading to

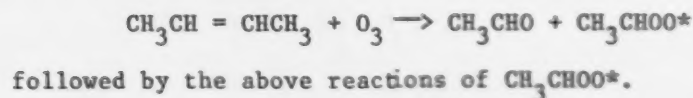


and thus

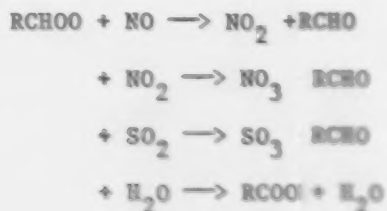


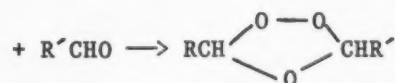
We note that the radical yields from the ethene- O_3 and propene- O_3 reactions are $0.12 HO_2^{\cdot}$ radicals per ethene molecule reacted and $0.205 HO_2^{\cdot} + 0.095 OH^{\cdot} + 0.025 CH_3O^{\cdot} + 0.215 C_3O_2^{\cdot}$ per propene molecule reacted.

Finally, for trans-2-butene, we have



The thermalized Criege intermediates are then available to react with other molecules in the system,

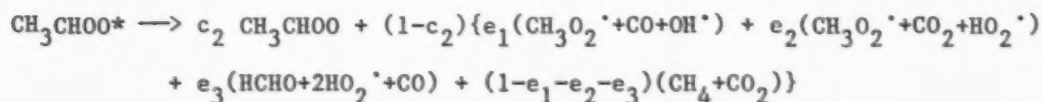




Consider now the propene- O_3 reaction:



The 50-50 split is assumed in virtually all current reaction mechanisms. Niki et al. (1977) studied the dynamics of CH_3CHOO^* , and found 18 percent stabilization, whereas a value of 40 percent is assumed in the ALW mechanism. We can express the fate of CH_3CHOO^* as



where c_2 is the fraction of stabilization of CH_3CHOO^* . The product distribution splits assumed in the mechanisms we have been studying are given in Table 19. We see that the values of e_1 , e_2 and e_3 used in the ALW and KW mechanisms are:

	e_1	e_2	e_3
ALW	0.33	0.33	0.05
KW	0.34	0.425	0.05

We note that the Criegee intermediate decomposition in the KW mechanism, which occurs at an overall rate of 10^3 min^{-1} , in the proportions shown in Table 19, is competitive with its reaction with $CARB$, NO and HO_2 . Because decomposition is competitive with reaction, the fraction of stabilization depends on the concentrations of the species with

TABLE 19

Alkene-O₃ Reactions in the Lumped Mechanisms

MECHANISM	REACTIONS
Atkinson et al. (1982) (ALW)	$\text{PROPENE} + \text{O}_3 \longrightarrow 0.5 \text{ HCHO} + 0.5 \text{ CH}_3\text{CHO} + 0.2 \text{ H}_2\text{COO} + 0.2 \text{ CH}_3\text{CHOO}$ $+ 0.3 \text{ CO} + 0.2 \text{ HO}_2 + 0.1 \text{ OH} + 0.2 \text{ CH}_3\text{O}_2$ $\text{BUTENE} + \text{O}_3 \longrightarrow \text{CH}_3\text{CHO} + 0.4 \text{ CH}_3\text{CHOO} + 0.2 \text{ CO}$ $+ 0.2 \text{ OH} + 0.3 \text{ HO}_2 + 0.45 \text{ CH}_3\text{O}_2$
Demerjian (1982)	$\text{HCl} + \text{O}_3 \longrightarrow \text{HC}_3 + \text{RO}_2 + \text{HO}_2$
McRae and Seinfeld (1978) (MS)	$\text{OLE} + \text{O}_3 \longrightarrow 0.5 \text{ RCHO} + 0.5 \text{ HCHO} + 0.304 \text{ HO}_2$ $+ 0.306 \text{ RO}_2 + 0.136 \text{ OH} + 0.034 \text{ RO}$
Killus and Whitten (1982) (KW)	$\text{ETH} + \text{O}_3 \longrightarrow \text{CARB} + \text{CRIG}$ $\text{CRIG} \longrightarrow \text{H}_2\text{O} + \text{CO} \quad (67\%)$ $\longrightarrow \text{stable products} \quad (24\%)$ $\longrightarrow 2\text{HO}_2 + \text{CO} \quad (9\%)$ $\text{CRIG} + \text{NO} \longrightarrow \text{NO}_2 + \text{CARB}$ $\text{CRIG} + \text{NO}_2 \longrightarrow \text{NO}_3 + \text{CARB}$
Penner and Walton (1982) (PW)	$\text{HCl} + \text{O}_3 \longrightarrow \text{HC4} + 0.5 \text{ HO}_2$

which CRIG reacts. Using the rate constants of the mechanism, that fraction is given by

$$f = \frac{1.2 \times 10^4 [\text{NO}] + 8 \times 10^3 [\text{NO}]}{10^3 + 1.2 \times 10^4 [\text{NO}] + 8 \times 10^3 [\text{NO}_2]}$$

For example, if $[\text{NO}] = [\text{NO}_2] = 0.1$ ppm, $f = 0.67$, whereas if $[\text{NO}] = [\text{NO}_2] = 0.01$ ppm, $f = 0.167$. The KW mechanism involves a similar treatment of the OLE-O_3 reaction.

We see that the ALW mechanism is based on the general Criegee mechanism given earlier with $k_4 = 0$, i.e. a certain fraction of the energetic Criegee intermediates is assumed to decompose immediately into stable products, the remainder being then available to react with other species in the system. The fraction stabilized is assumed to be 0.4 for both H_2COO and CH_3CHOO ; in the latter case, this fraction is high when compared to the single available experimental value of 0.18. In the KW mechanism, on the other hand, 100 percent stabilization is assumed to occur immediately, and thus $k_2 = 0$. The stabilized Criegee intermediate then may either decompose into stable products or react with other species in the system. The rate constant for decomposition is fixed at 1000 min^{-1} , so that, as shown above, the amount of Criegee intermediate actually decomposing depends on the concentration of other species. Although the available experimental data concerning the fate of Criegee intermediate tend to support the idea that the energetic intermediate first either decomposes or is stabilized, the quantity of such data is insufficient to draw a definite conclusion concerning

which approach to representing Criegee intermediate chemistry is, in fact, the more justifiable.

Of the alkene- O_3 reactions in the three generalized species mechanisms, assuming equal rate constants, the Demerjian mechanism is most "reactive," predicting two peroxy radical products, in addition to the aldehyde product specified in all mechanisms, whereas the PW mechanism is least "reactive" with only 0.5 peroxy radicals formed per alkene- O_3 reaction. The MS mechanism lies intermediate between the other two in reactivity with about 0.78 radicals formed per O_3 attack. In the MS mechanism, 80 percent of the Criegee intermediate is assumed to decompose, the other 20 percent going to non-radical products. The assumptions leading to the radical products in the Demerjian and PW mechanisms have not been discussed in their mechanism descriptions. We recall that in the ALW mechanism, 60 percent of the Criegee intermediate is assumed to decompose, with the remaining 40 percent reacting as a peroxy radical, whereas in the KW mechanism, about 85 percent of the intermediate is assumed to decompose although that decomposition is competitive with other reactions.

In summary, we note that each of the five lumped mechanisms treats the alkene- O_3 reaction somewhat differently, leading to different "reactivities" of the steps. From the distribution of radical products one can obtain a qualitative indication of the relative order of reactivity of the alkene- O_3 reaction steps, although different assumptions concerning the reaction paths of the Criegee intermediate

make it difficult to make precise comparisons without detailed computations.

3.4 Aromatic Photooxidation Chemistry

The only important atmospheric oxidation pathway for aromatic hydrocarbons is reaction with OH. Current understanding concerning aromatic photooxidation chemistry has been summarized by Atkinson and Lloyd (1983) and Killus and Whitten (1982b).

3.4.1 Toluene-OH Reaction

The toluene-OH reaction proceeds by both abstraction and addition pathways. Figure 8 shows the toluene-OH abstraction mechanism including benzaldehyde chemistry, and Figure 9 presents a summary of a proposed toluene-OH addition mechanism.

3.4.2 m-Xylene-OH Reaction

m-Xylene chemistry is similar to toluene chemistry, with approximately 96 percent of the initial OH attack proceeding via addition. A summary of the addition pathway is shown in Figure 10.

3.4.3 Treatment of Aromatic Photooxidation by the ALW Mechanism

The ALW mechanism treats benzene chemistry explicitly, uses toluene to represent monoalkylbenzenes, and uses a lumped average xylene to represent di- and tri-alkylbenzenes.

It has been found experimentally that the fraction of the initial OH reaction proceeding by abstraction has the following approximate values:

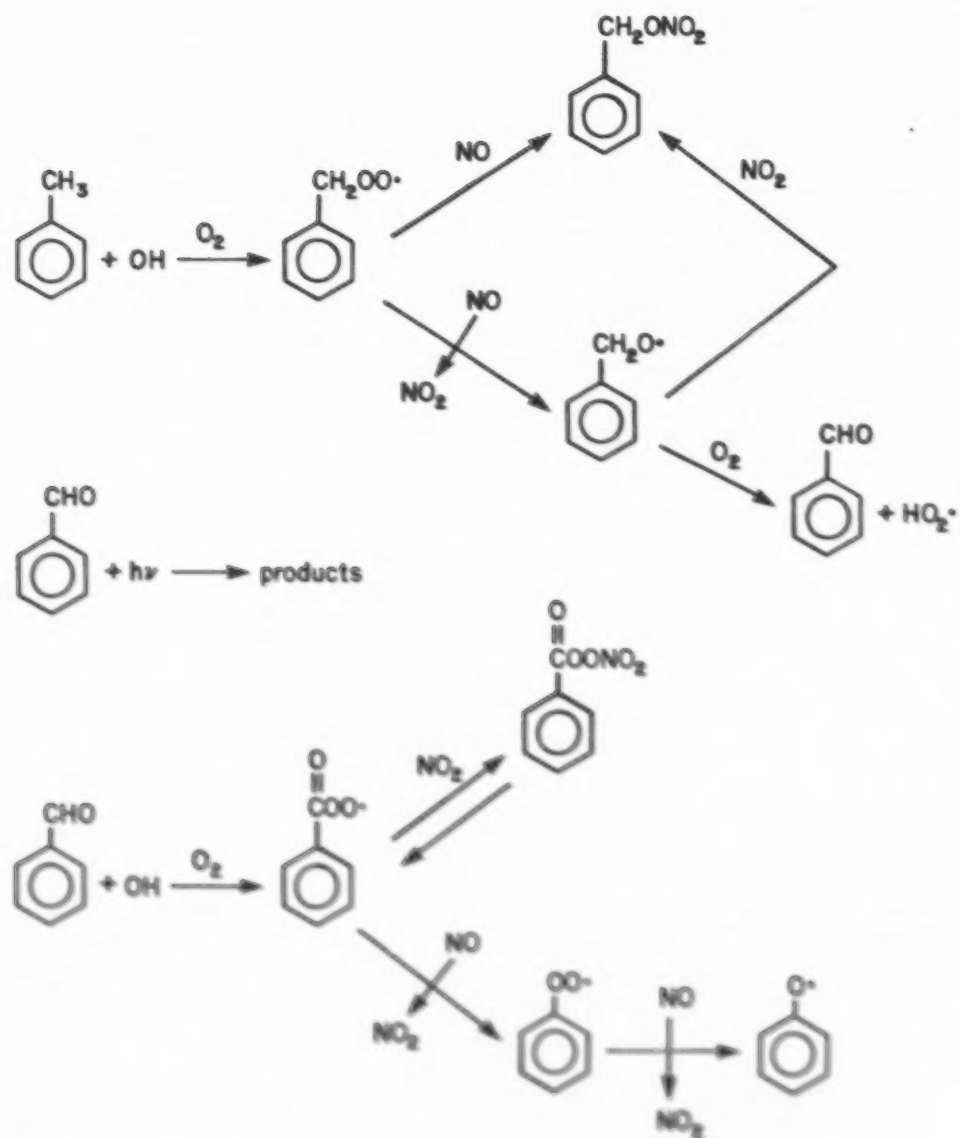


Figure 8. Toluene-OH abstraction pathway reaction mechanism

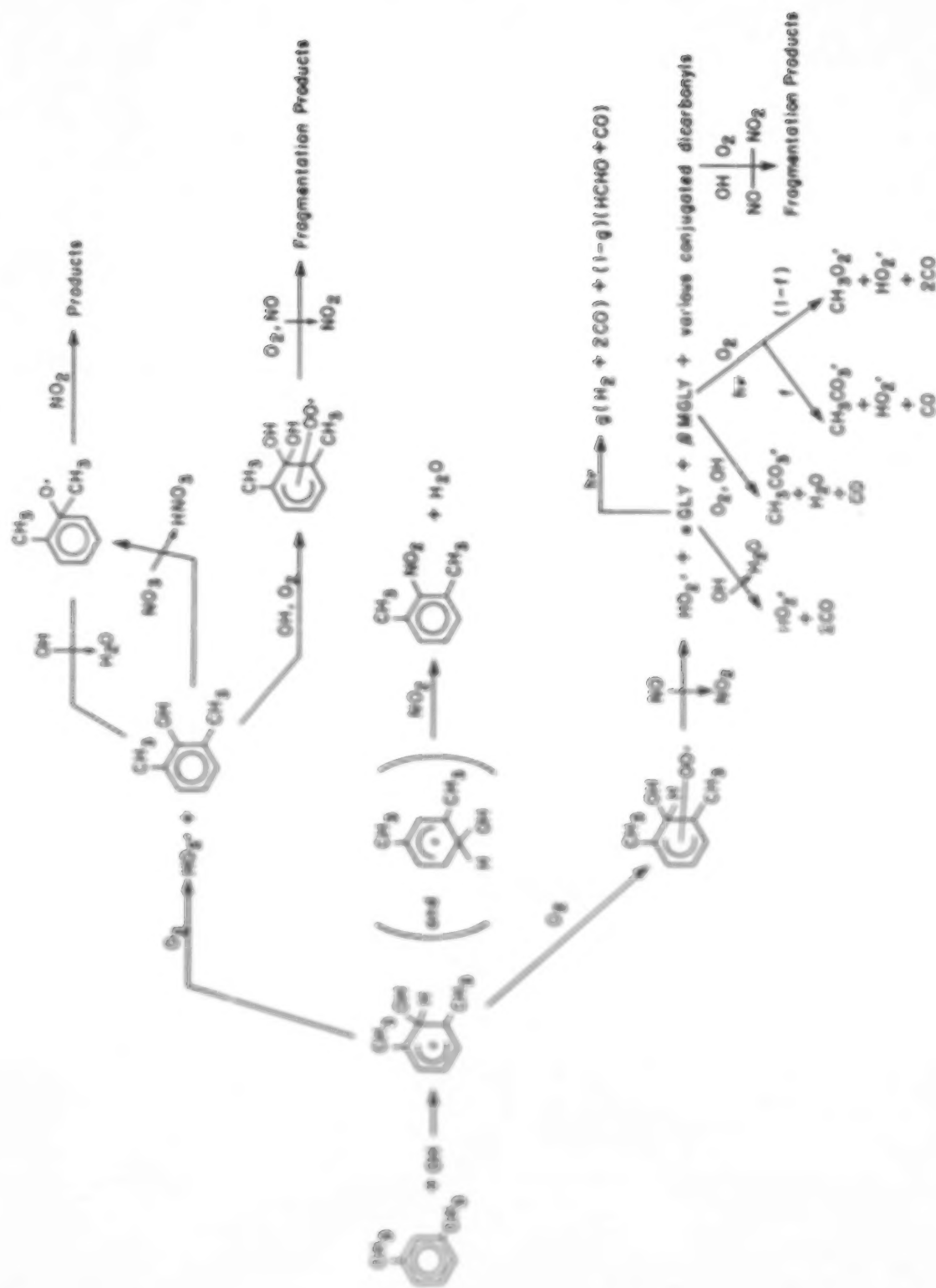


Figure 10. m-Xylene-OH addition pathway reaction mechanism

GLY = glyoxal

MGLY = methylglyoxal

- 0.1 for toluene
- < 0.05 for benzene
- 0.2 for o-xylene
- 0.04 for m-xylene
- 0.07 for p-xylene

In the ALW mechanism, the abstraction fraction is 0.15 for toluene, but 0 for benzene and xylene. ALW also assume no m-nitrotoluene formation and 25 percent cresol formation, and therefore 75 percent adduct formation. No distinction is made between benzene, toluene and xylene with regard to cresol formation. Thus, although benzene yields phenol and the xylenes form dimethyl phenol, the mechanism represents these species by o-cresol.

The initial step can therefore be written as



or, simplifying,



For benzene and the di- and tri-alkylbenzenes, the ALW mechanism employs



In all three of the above reactions, the toluene-OH-O₂ adduct is represented by the single species ADD. Differences in the adducts

formed from toluene, benzene and xylene are incorporated into the reactions of the ADD species.

In the abstraction pathway it is assumed that 25 percent of the aromatic peroxy radicals add NO to form nitrates. (Recent evidence suggests that this percentage is probably substantially lower (Leone and Seinfeld, 1983a)). Thus, the ALN mechanism includes the reaction

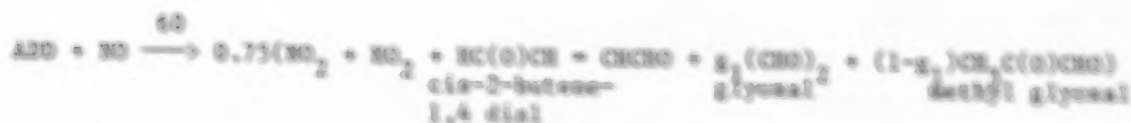


Benzaldehyde photolysis is represented as



where non-radical products are assumed.

In the addition pathway, the adduct-NO reaction is represented by



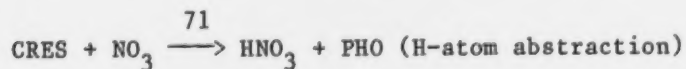
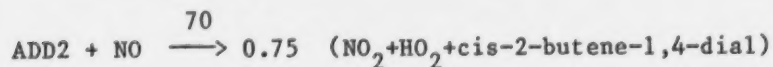
where the factor 0.75 arises from assuming that 25 percent of the adducts form nitrates that do not react further. The fraction g_1 is used to account for the different forms of the adducts formed from benzene, toluene, and xylene. It has been proposed that the dicarbonyls are produced as follows:



Thus, the ALW mechanism employs

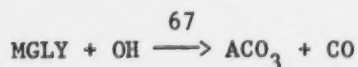
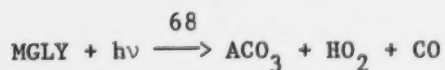
$$g_1 = \frac{k_2[\text{BEN}] + 0.1k_3[\text{XYL}]}{k_1[\text{TOL}] + k_2[\text{BEN}] + k_3[\text{XYL}]}$$

The ALW mechanism uses o-cresol to represent the chemistry of all phenolic species (phenol, cresols, and dimethyl phenols). The reactions employed are

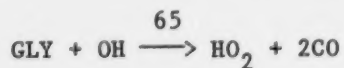


where PHO represents the various oxy radicals, and 25 percent nitrate formation is assumed in reaction 70.

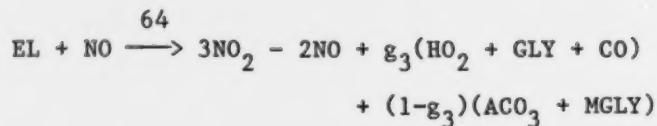
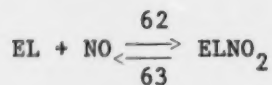
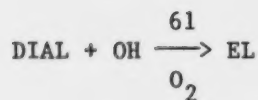
The ALW mechanism treats methyl glyoxal photolysis and the methyl glyoxal-OH reaction explicitly,



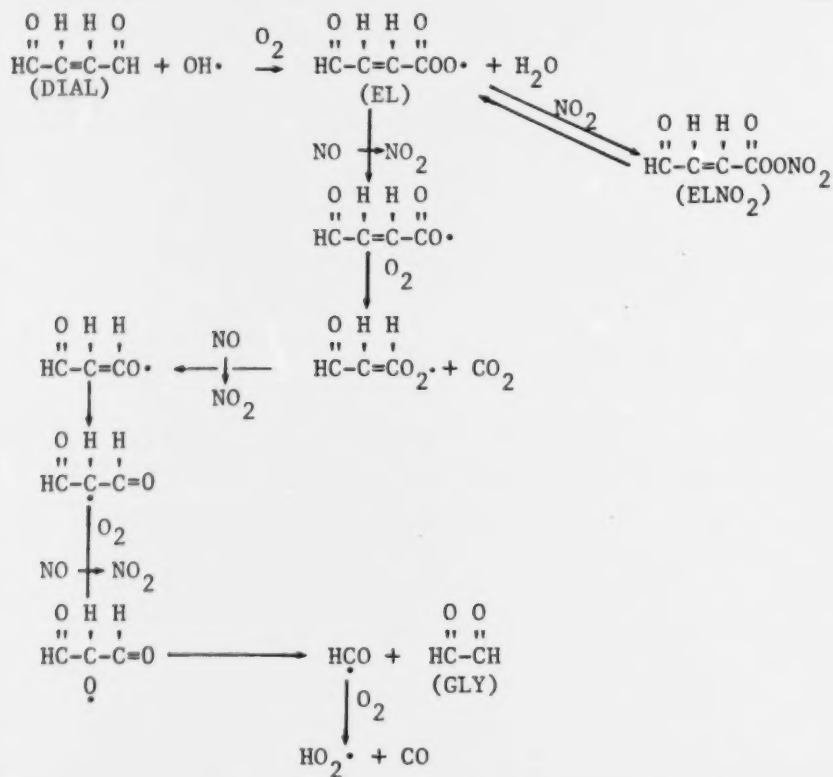
The glyoxal reactions are represented by



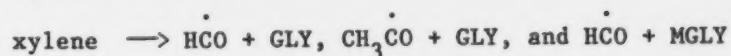
The chemistry of the conjugated- γ -dicarbonyls is represented by



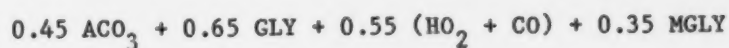
The rationale behind this reaction sequence is as follows:



The predicted product yields from the three aromatic classes considered are:



The estimated average composition of products from a lumped xylene species is



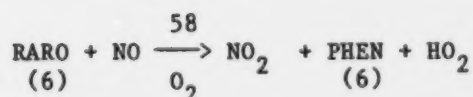
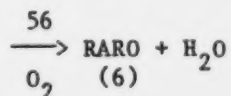
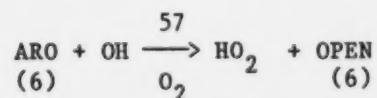
based on which the ALW mechanism assumes a product distribution of $0.5(\text{ACO}_3 + \text{GLY} + \text{HO}_2 + \text{CO} + \text{MGLY})$. Consequently, g_3 is given by

$$g_3 = \frac{k_1[\text{TOL}] + k_2[\text{BEN}] + 0.5k_3[\text{XYL}]}{k_1[\text{TOL}] + k_2[\text{BEN}] + k_3[\text{XYL}]}$$

3.4.4 Treatment of Aromatic Photooxidation by the KW Mechanism

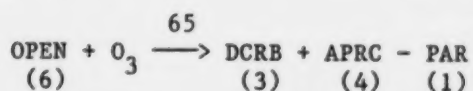
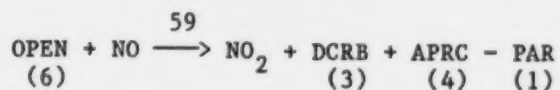
The basic lumped aromatic unit in the KW mechanism is the species ARO which contains six carbon atoms and represents the benzene ring. For example, then, toluene = 1 ARO + 1 PAR, and xylene = 1 ARO + 2 PAR.

The initial reactions in the KW mechanism are

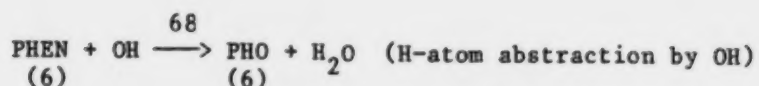


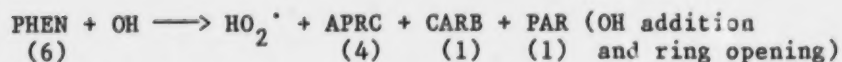
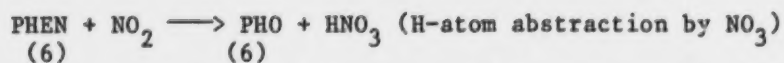
$$\text{CH}_3\text{C}_6\text{H}_5 + \text{OH} \xrightarrow{\text{O}_2} \text{CH}_2\text{C}_6\text{H}_5\text{OO}^\bullet + \text{H}_2\text{O}$$
$$\text{PAR} + \text{OH} \longrightarrow \text{MEO}_2 + \text{H}_2\text{O}$$

There are two ring opening reactions employed in the KW mechanism.



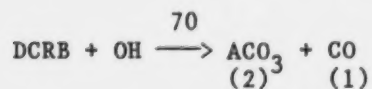
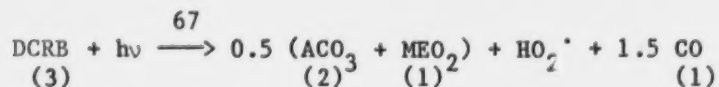
Reactions of the phenolic compounds are represented by



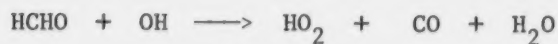
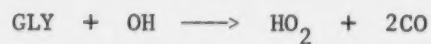


where PHO represents various oxy radicals.

The chemistry of methyl glyoxal and biacetyl is represented by the two reactions

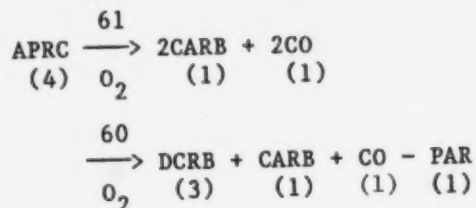


Glyoxal is represented as 1 CARB + 1 CO, based on the similarity between the glyoxal-OH reaction and the formaldehyde-OH reaction:



The relation $\text{GLY} = \text{CARB} + \text{CO}$ is then evident when reactions a and b are compared.

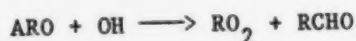
The chemistry of APMC is represented in the KW mechanism by the two reactions,



3.4.5 Evaluation of the Aromatic Hydrocarbon Reactions in the Generalized Species Mechanisms

The Demerjian, MS and PW lumped mechanisms employ simple reaction schemes to describe the photooxidation of aromatic hydrocarbons. The success of these short reaction schemes depends on how well they simulate the radical formation processes occurring in aromatic systems, because it is the formation of radicals which brings about the conversion of NO to NO₂.

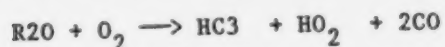
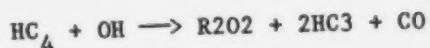
The MS mechanism relies on a single reaction step to describe the chemistry of aromatic compounds



Because only one step is included, it must account for both the decay of the initial aromatic species and the formation of radicals. To perform both of these functions accurately, and in one step, is difficult.

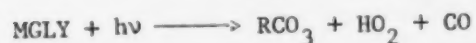
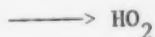
For example, in the aromatic portion of the ALW mechanism one or another radical species is formed at 20 different points.

The Demerjian mechanism includes three steps to describe atmospheric aromatic chemistry.



where HC4 represents aromatics, HC3 aldehydes, R2O2 is a peroxy radical, and R2O is an alkoxy radical. The main difference between this mechanism and the MS mechanism is that the peroxy and alkoxy radicals formed from the aromatic hydrocarbons (R2O2 and R2O) are distinguished from those formed in the alkane and alkene portion of the mechanism.

PW use five steps in the aromatic portion of their mechanism,



where BRO2OHHH represents the aromatic radical which undergoes ring scission, MGLY represents methylglyoxal, and RCO_3 the peroxyacyl radical. The advantages of this reaction scheme relative to the earlier two are that it accounts for both the cresol formation and ring opening pathways of the addition reaction and it includes the formation of the important α -dicarbonyl, methyl glyoxal.

It is clear that the aromatic portions of the Demerjian, MS and PW mechanisms require an updating to reflect information that has become available since their original formulation. Moreover, it

appears that such abbreviated aromatic mechanisms as currently exist in these three mechanisms are inconsistent with the level of detail accorded to the other aspects of the overall photochemistry, especially in light of the relative importance of aromatic compounds in the total atmospheric hydrocarbon mix.

CHAPTER 4

SPECIFICATION OF PHOTOLYSIS RATE CONSTANTS

One of the most important processes that influences the species concentration dynamics observed in the atmosphere or in smog chambers is the dissociation of photochemically active reactants. This chapter presents a comparison of approaches used in specifying the photolysis rate constants in the mechanisms. The objective of this work is to summarize, in one convenient location, all the documentation needed to reproduce the values used in the six mechanisms introduced in Chapter 2.

4.1 Methods for the Determination of Photolysis Rate Constants

In most photochemical mechanisms the photodissociation reactions are typically represented by steps of the form



where X_i denotes species i , and k_i the associated rate constant.* As shown in Table 20 there are substantial differences both in terms of the number of species and photolysis steps used in each of the mechanisms. In addition these disparities are compounded by significant variations in the magnitude of the rate constants.

* When discussing photolysis reactions, we will use the notation k_i to denote the rate constant for photolysis of species i . Ordinarily k_i refers to reaction number i .

TABLE 20

Summary of Photolysis Reaction Steps From Mechanism Survey

PHOTOLYSIS STEP ^(a)	REACTION MECHANISM ^(b)					
	1	2	3	4	5	6
$\text{NO}_2 + \text{h}\nu \longrightarrow \text{NO} + \text{O}(^3\text{P})$	*	*	*	*	*	*
$\text{HONO} + \text{h}\nu \longrightarrow \text{OH} + \text{NO}$	*	*	*	*	*	*
$\text{H}_2\text{O}_2 + \text{h}\nu \longrightarrow 2\text{OH}$	*	*	*		*	*
$\text{NO}_3 + \text{h}\nu \longrightarrow \text{NO}_2 + \text{O}(^3\text{P})$	*					*
$\longrightarrow \text{NO} + \text{O}_2$	*					*
$\text{N}_2\text{O}_5 + \text{h}\nu \longrightarrow 2\text{NO}_2 + \text{O}$						*
$\text{O}_3 + \text{h}\nu \longrightarrow \text{O}_2 + \text{O}(^3\text{P})$	*		*		*	*
$\longrightarrow \text{O}(^1\text{D}) + \text{O}_2(^1\text{g})$		*	*	*		*
$\text{HCHO} + \text{h}\nu \longrightarrow \text{CO} + \text{H}_2$	*	*	*		*	
$\longrightarrow \text{HCO} + \text{H}$	*				*	
$\text{CH}_3\text{CHO} + \text{h}\nu \longrightarrow \text{CH}_4 + \text{CO}$	*		*			
$\longrightarrow \text{HCO} + \text{CH}_3$	*		*			
$\text{RCHO} + \text{h}\nu \longrightarrow \text{CO} + \text{a}_1\text{HO}_2 + \text{a}_2\text{RO}_2$	*	*	*		*	*
$\text{CARB} + \text{h}\nu \longrightarrow \text{b}_1\text{HO}_2 + \text{b}_2\text{MEO}_2 + \text{b}_3\text{CO} + \text{b}_4\text{X}$					*	
$\text{DCRB} + \text{h}\nu \longrightarrow \text{c}_1\text{HO}_2 + \text{c}_2\text{MEO}_2 + \text{c}_3\text{ACO}_2 + \text{c}_4\text{CO} + \text{X}$					*	
$(\text{CHO})_2 + \text{h}\nu \longrightarrow \text{HCHO} + \text{CO}$	*					
$\text{CH}_3\text{COCH}_3 + \text{h}\nu \longrightarrow \text{CH}_3\text{CO}_3 + \text{C}_2\text{H}_5\text{O}_2$	*					
$\text{CH}_3\text{COCHO} + \text{h}\nu \longrightarrow \text{HO}_2 + \text{RCO}_3 + \text{CO}$	*					*
$\text{CH}_3\text{COC}_2\text{H}_5 + \text{h}\nu \longrightarrow \text{CH}_3\text{CO}_3 + \text{C}_2\text{H}_5\text{O}_2$	*					
$\text{RONO} + \text{h}\nu \longrightarrow \text{NO} + \text{RO}$					*	

Footnotes for Table 20

- (a) Only the initial products of the photolysis steps are shown in the above Table. Many of the mechanisms combine elementary reaction steps and eliminate product species that have very short lives.

Footnotes for Table 20 (Continued)

(b) Reaction Mechanisms

1	Atkinson et al. (1982)	-	Table 22
2	Demerjian (1982)	-	Table 27
3	Dodge (1977)	-	Table 26
4	Killus and Whitten (1982a)	-	Table 24
5	McRae and Seinfeld (1983)	-	Table 25
6	Penner and Walton (1982)	-	Table 28

How closely the kinetics of the photodissociation step can reproduce the concentration dynamics of X_i is closely tied to the accuracy with which the rate constant k_i can be specified. Depending on the particular application one of two basic methods are usually used to establish the photolysis rates. The most direct way is to measure rates with chemical actinometers. In this approach the species of interest is isolated and allowed to photolyze under controlled conditions in either a flow or batch reactor. From a knowledge of the initial concentration, the exposure time and the resulting product distribution the photolysis rate can be calculated for the particular radiation conditions.

In smog chamber studies the NO_2 photolysis is often determined by using a quartz flow reactor in which a continuous stream of NO_2 is photolysed in a co-flowing stream of nitrogen (Pitts et al. 1976). By monitoring the NO concentration level in the effluent it is possible to determine the NO_2 photolysis rate. Chemical actinometers have also been used to determine NO_2 photolysis rates under atmospheric conditions (Zafonte et al., 1977 and Stedman et al., 1977). These experiments have usually only been carried out for limited time periods. Fortunately these investigators correlated their results against concurrent measurements of the solar radiation in the ultraviolet (uv) portion of the spectrum. Radiometric data were obtained with Eppley ultraviolet pyranometers that have a full bandwidth sensitivity of 295-385 nm, a wavelength interval relevant to many photochemical reactions. Provided that the spectral distribution of the radiation remains

constant, the results of the correlations provide a direct means of determining the NO_2 photolysis rate from a knowledge of solar radiation measurements. A similar methodology has been employed by Pitts et al. (1976) to report smog chamber photolysis rates. While chemical actinometry offers the most direct means for determining rate constants, the technique has unfortunately only been applied to determine the photolysis rates of a few species, principally NO_2 and HCHO .

In smog chambers as well as in atmospheric applications photolysis rates are needed for a much larger number of species. The method that is usually applied in these circumstances is to calculate the rates from a knowledge of the spectral distribution of the photolyzing radiation and the properties of the molecule itself. If the concentration of the species X_i is low enough that it does not significantly affect the transfer of radiation then photolytic rate constant k_i can be calculated from

$$k_i = \sum_{\lambda = 290 \text{ nm}}^{800 \text{ nm}} \sigma_i \phi_i I \quad (4.1)$$

where $\sigma_i(\lambda)$ (cm^2) is the molecular absorption cross section for species i , $\phi_i(\lambda)$ is the quantum yield, and I is the actinic irradiance (photons $\text{cm}^{-2}\text{-s}^{-1}$), the radiometric energy incident on single molecules and, as conventionally defined, applies to ultraviolet wavelengths. In addition to wavelength, σ_i and ϕ_i depend on temperature. The actinic irradiance is typically obtained from either mathematical models of atmospheric radiative transfer or direct monochromator measurements of the spectral distribution. Demerjian et al. (1980), for example, have

published the data needed to evaluate (4.1) for a range of species likely to be encountered in atmospheric modeling applications.

4.2 Specification of the Actinic Irradiance

Since the wavelength-dependent absorption cross-sections and quantum yields are fixed, the variation of the species photolysis rate constant in space and time depends primarily on the variation of actinic flux. This parameter is very difficult to estimate from customary solar radiation measurements; in particular those made with broad band 180° pyroheliometers. As a result most photolysis rate constants are based on theoretical calculations of the solar flux in the spectral band of interest.

Compared to the total solar spectrum, the wavelength interval of interest in photochemical modeling applications is quite small ($290 \leq \lambda \leq 800$ nm), since solar radiation of wavelengths less than 290 nm does not reach the troposphere. The upper limit for the summation in (4.1) is set either by the reduction in species cross-section or quantum yield as a function of increasing wavelength.

Many previous modeling studies have employed the photolysis rate tabulations of Leighton (1961). His results were based on a radiative transfer calculation which, by necessity, employed many simplifying assumptions. The availability of more sophisticated radiative transfer models and more recent measurements of the upper atmospheric properties has led to considerable refinement in the calculation of solar fluxes. Penner and Walton (1982) used the model of Luther and Gelinas (1976) as

a basis for determining ultraviolet fluxes. In the Atkinson et al. (1982), Demerjian (1982), Killus and Whitten (1982a) and McRae and Seinfeld (1983) mechanisms the actinic irradiance is based on Demerjian et al. (1980). The results reported by Demerjian et al. (1980) are based on the calculations by Peterson (1976) using the computer program developed by Braslau and Dave (1973ab), which includes aerosol scattering and absorption, Rayleigh scattering, and ozone absorption. The atmospheric state assumed in the model corresponds to annual average U.S. urban conditions, corresponding to a cloud-free atmosphere over a typical urban environment. The actinic irradiance, at a particular time and elevation, is usually specified as a function of the solar zenith angle Z . For example, the zenith angle variation of the NO_2 photolysis rate, calculated using the methodology of Demerjian et al. (1980), is shown in Table 21.

4.3 Scaling of Photolysis Rates in Atmospheric Applications

Most theoretical calculations of the photolysis rate constants assume 'clear sky' conditions. Besides its diurnal variation, the actinic flux is sensitive to changes in surface albedo, amount of O_3 in the air column, cloudiness, surface elevation, atmospheric aerosol concentrations, and altitude above the surface (Peterson et al., 1977). In most cases the photolysis rates used in photochemical mechanisms have been calculated using ground level actinic irradiance data. Within the lowest 5-10 km of the atmosphere the actinic flux increases with elevation which in turn leads to higher photolysis rates. The results of Demerjian et al. (1980) and Peterson et al. (1977), for NO_2

TABLE 21

Nitrogen Dioxide Photolysis Rate as a function of Zenith Angle

ZENITH ANGLE (z°)	PHOTOLYSIS RATE (min^{-1})	RATE RELATIVE TO $z=0^\circ$
0	0.533	1.000
10	0.529	0.992
20	0.515	0.966
30	0.493	0.925
40	0.457	0.857
50	0.403	0.756
60	0.329	0.617
70	0.214	0.402
78	0.105	0.197
86	0.023	0.043
90	0.000	0.000

Source: Demerjian et al. (1980)

and HCHO show a significant increase with height. For example, at an elevation of 0.98 km the photolysis rate for these species, at a zenith angle of 0° , is approximately 20% higher than the corresponding ground level value. This suggests that the photolysis rates need to be adjusted if the region being studied is at a high elevation.

One additional problem that is encountered in practical applications is how to modify the calculated results when there is a perturbation to the basic atmospheric state employed in the radiative transfer calculations. Increased aerosol loadings or the presence of clouds would require scaling of the photodissociation rates. For example, Penner and Walton (1982) adjust their photolysis rates to account for the presence of clouds or aerosols in the surface layer. When only broad-band measurements of solar radiation are available, the correction of the calculated values can be based on the ratio of pyranometer observations to the theoretical clear sky transmission. One important point to note is that scalings based on total solar fluxes may not provide a good representation of the variation in the ultraviolet (uv) flux density. The reason for this is the total solar fluxes are not strongly influenced by cloud and aerosols. On the other hand, the ultraviolet fluxes are markedly attenuated by any increase in scattering. Despite these caveats a crude estimate of the NO_2 photolysis rate constant can be developed by scaling the calculated value of k_1 against the measured total solar radiation flux TSR. By combining routine monitoring data, collected in Los Angeles, with the theoretical results of Demerjian et al. (1980) for the same location the relationship between

the photolysis rate and the total flux is given by

$$k_1 (\text{min}^{-1}) = 0.4 \text{ TSR } (\text{cal-cm}^{-2}\text{-min}^{-1}) \quad (4.2)$$

In situations where ultraviolet pyranometer data are available another approach is possible. As described previously, Zafonte et al. (1977) and Stedman et al. (1977) plotted their NO_2 photodissociation rates against measurements of solar radiation in the ultraviolet portion of the spectrum. Their results provide a direct means for scaling calculated photolysis rates. The scale factor applied to the theoretical estimates is simply the ratio of the measured and calculated actinic irradiances. Schere and Demerjian (1977) used ultraviolet measurements and the calculated clear solar fluxes to scale the rate constants, with the ultraviolet scaled photolysis rates closely matching the results obtained using a chemical actinometer.

Photochemical smog production depends on ultraviolet radiation differently at the short (300-330 nm) wavelength region than at the long (360-400 nm) wavelength part of the ultraviolet. The smog production rate is more sensitive to the shorter wavelengths (Winer et al., 1979). Although NO_2 photolysis has been the measure of smog potential, measurements using UV-B filters which characterize only the shorter wavelengths would be useful. This part of the spectrum (239-330 nm) characterizes aldehyde photolysis to which smog production is sensitive.

4.4 Specification of Mechanism Photolysis Rate Constants

In atmospheric modeling applications the photolysis rates are usually established by evaluating the summation (4.1) for each of the species of interest. One of the first applications of this method was the pioneering work of Leighton (1961). More recently, Gelinas et al. (1974), Schere and Demerjian (1977) and Demerjian et al. (1980) have developed computer programs that enable the direct calculation of the photolysis rates given the actinic irradiance, quantum yields and absorption cross-sections. While the availability of these algorithms considerably reduces the computational burden, there has, unfortunately, been no attempt at standardization of the necessary input information. The objective of this section is to document the procedures and literature sources used in developing the rate constants for each of the mechanisms.

In the current version of the Atkinson et al. (1982) mechanism, the species absorption cross-sections and quantum yield data are based on the results from the review of Atkinson and Lloyd (1983). The actinic irradiance data of Demerjian et al. (1980) were used by Lurmann (1982) to calculate the photolysis rates shown in Table 22. Each rate has been scaled relative to the NO_2 value to facilitate comparisons of these rates among different reaction mechanisms. Since the NO_2 rates used in the Atkinson et al. (1982) mechanism are identical to those of Demerjian et al. (1980) the absolute magnitude of the NO_2 photolysis rate, as a function of the zenith angle, can be obtained from Table 21. Diurnal variations in the photolysis rates of most species can be

TABLE 22

Photolysis Reaction Steps in the Atkinson et al. (1982)
Photochemical Reaction Mechanism^a

REACTION NUMBER	PHOTODISSOCIATION STEP ^(b)	PHOTOLYSIS RATE ^(c) RELATIVE TO NO ₂
1	NO ₂ + hv → NO + O(³ P)	1.0
3	O ₃ + hv → 2OH	4.20x10 ⁻⁸ [H ₂ O] ^(d)
6	HONO + hv → OH + NO	1.70x10 ⁻¹
11	H ₂ O ₂ + hv → 2OH	7.10x10 ⁻⁴
18	NO ₃ + hv → 0.3NO + 0.7NO ₂ + 0.7O ₃	1.55x10 ¹
21	HCHO + hv → 2HO ₂ + CO	3.50x10 ⁻³
22	HCHO + hv → CO + H ₂	3.40x10 ⁻³
24	CH ₃ CHO + hv → CH ₃ O ₂ + HO ₂ + CO	8.40x10 ⁻⁴
39	RCHO + hv → C ₂ H ₅ O ₂ + CO + HO ₂	8.40x10 ⁻⁴
42	MEK + hv → CH ₃ CO ₃ + C ₂ H ₅ O ₂	1.70x10 ⁻³
43	CH ₃ COCH ₃ + hv → CH ₃ CO ₃ + CH ₃ O ₂	1.70x10 ⁻⁴
67	(CHO) ₂ + hv → HCHO + CO	1.00x10 ⁻¹⁰
69	CH ₃ COCHO + hv → CH ₃ CO ₃ + HO ₂ + CO	1.50x10 ⁻¹
75	ARCHO + hv → Products	4.50x10 ⁻³

Footnotes for Table 22

(a) Mechanism documentation: Atkinson et al. (1979, 1982), Carter et al. (1979)
The particular values selected for the species absorption cross-sections and quantum yields are described in Atkinson and Lloyd (1983).

(b) RCHO - Higher aldehydes ≥ C₃
MEK - Methyl ethyl ketone (CH₃COC₂H₅)
ARCHO - Benzaldehyde
Products - Non reactive reaction products
(CHO)₂ - Glyoxal

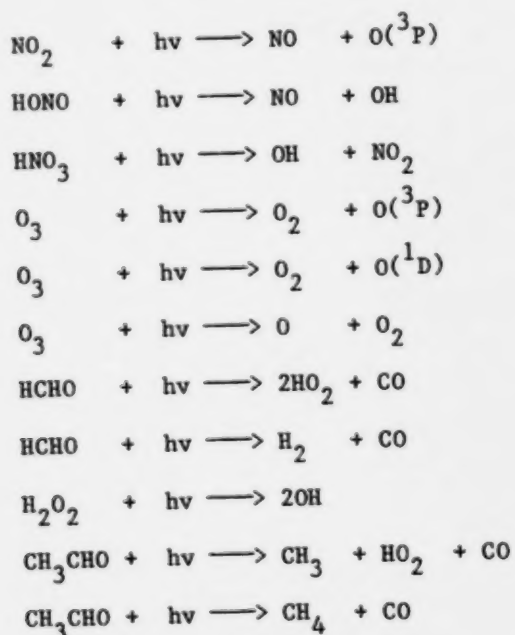
Footnotes for Table 22 (Continued)

(c) The photolysis rates have been scaled relative to the NO_2 value however, for the species O_3 , HCHO and CH_3CHO the scaling is a function of the zenith angle. Table 23 gives the scale parameters for these species.

(d) $[\text{H}_2\text{O}]$ in ppm.

determined by applying the scale factors to the corresponding NO_2 rate. For the species O_3 , HCHO and CH_3CHO , the scaling, as shown in Table 23, is a function of the zenith angle.

Killus and Whitten (1982a) and McRae and Seinfeld (1983) primarily base their mechanism photolysis rates on the work of Demerjian et al. (1980). Since this is perhaps the most widely used procedure for calculating the diurnal variations in photolysis rates it is useful to describe the underlying basis of the method. Demerjian et al. (1980) carried out an extensive literature survey and collected the data needed to calculate the photolysis rates for the following eleven reactions of interest in atmospheric modeling applications.



For each species and reaction pathway they tabulated the absorption cross-sections and quantum yields in 10 nm wavelength increments over the range 290 to 800 nm. The actinic flux used by Demerjian et al.

TABLE 23

Photolysis Scaling Ratios Relative to NO_2 Rate for the
Atkinson et al. (1982) Photochemical Reaction Mechanism^a

ZENITH ANGLE ($^\circ$)	PHOTOLYSIS SCALING RATIOS RELATIVE TO NO_2			
	$\text{O}_3 + h\nu \rightarrow^{(b)}$	$\text{HCHO} + h\nu \rightarrow \text{H}_2$	$\text{HCHO} + h\nu \rightarrow \text{H}^\cdot$	$\text{CH}_3\text{CHO} + h\nu \rightarrow \text{HCO}^\cdot$
0	4.20×10^{-8}	3.5×10^{-3}	3.4×10^{-3}	8.4×10^{-4}
10	4.10×10^{-8}	3.5×10^{-3}	3.4×10^{-3}	8.3×10^{-4}
20	3.80×10^{-8}	3.4×10^{-3}	3.4×10^{-3}	8.0×10^{-4}
30	3.30×10^{-8}	3.3×10^{-3}	3.3×10^{-3}	7.4×10^{-4}
40	2.60×10^{-8}	3.3×10^{-3}	3.2×10^{-3}	6.7×10^{-4}
50	1.90×10^{-8}	2.8×10^{-3}	3.0×10^{-3}	5.6×10^{-4}
60	1.20×10^{-8}	2.4×10^{-3}	2.8×10^{-3}	4.4×10^{-4}
70	6.20×10^{-9}	1.9×10^{-3}	2.5×10^{-3}	3.1×10^{-4}
78	3.00×10^{-9}	1.6×10^{-3}	2.2×10^{-3}	2.1×10^{-4}
84	1.30×10^{-9}	1.4×10^{-3}	2.2×10^{-3}	1.3×10^{-4}

Footnotes for Table 23

(a) The scaling ratios are based on modifications, by Lurmann (1982), of the zenith angle variations in photolysis rates presented in Demerjian et al. (1980). Given an NO_2 photolysis rate and the corresponding zenith angle this table can be used to establish the O_3 , HCHO and CH_3CHO rates.

(b) All values in this column should be multiplied by $[\text{H}_2\text{O}]$, in ppm.

TABLE 23

Photolysis Scaling Ratios Relative to NO_2 Rate for the
Atkinson et al. (1982) Photochemical Reaction Mechanism^a

ZENITH ANGLE ($^\circ$)	PHOTOLYSIS SCALING RATIOS RELATIVE TO NO_2			
	$\text{O}_3 + h\nu \rightarrow^{(b)}$	$\text{HCHO} + h\nu \rightarrow \text{H}_2$	$\text{HCHO} + h\nu \rightarrow \text{H}^\cdot$	$\text{CH}_3\text{CHO} + h\nu \rightarrow \text{HCO}^\cdot$
0	4.20×10^{-8}	3.5×10^{-3}	3.4×10^{-3}	8.4×10^{-4}
10	4.10×10^{-8}	3.5×10^{-3}	3.4×10^{-3}	8.3×10^{-4}
20	3.80×10^{-8}	3.4×10^{-3}	3.4×10^{-3}	8.0×10^{-4}
30	3.30×10^{-8}	3.3×10^{-3}	3.3×10^{-3}	7.4×10^{-4}
40	2.60×10^{-8}	3.3×10^{-3}	3.2×10^{-3}	6.7×10^{-4}
50	1.90×10^{-8}	2.8×10^{-3}	3.0×10^{-3}	5.6×10^{-4}
60	1.20×10^{-8}	2.4×10^{-3}	2.8×10^{-3}	4.4×10^{-4}
70	6.20×10^{-9}	1.9×10^{-3}	2.5×10^{-3}	3.1×10^{-4}
78	3.00×10^{-9}	1.6×10^{-3}	2.2×10^{-3}	2.1×10^{-4}
84	1.30×10^{-9}	1.4×10^{-3}	2.2×10^{-3}	1.3×10^{-4}

Footnotes for Table 23

(a) The scaling ratios are based on modifications, by Lurmann (1982), of the zenith angle variations in photolysis rates presented in Demerjian et al. (1980). Given an NO_2 photolysis rate and the corresponding zenith angle this table can be used to establish the O_3 , HCHO and CH_3CHO rates.

(b) All values in this column should be multiplied by $[\text{H}_2\text{O}]$, in ppm.

(1980) was obtained by solving a modified form of the numerical model developed by Braslau and Dave (1973ab). This information together with the species data was then used to determine the photolysis rates as a function of zenith angle and elevation above the surface.

At the time of the publication of Demerjian et al. (1980) there were substantial uncertainties associated with the quantum yields of acetaldehyde (CH_3CHO) and to a certain extent those of formaldehyde (HCHO). The most recent acetaldehyde rates, which are based on the recent quantum yield determinations of Horowitz and Calvert (1982) are a factor of two lower than the old values. In some cases, particularly for nitrous acid (HONO), hydrogen peroxide (H_2O_2) and the aldehydes there are almost factors of three difference between older and newer rates. The current versions of the Killus and Whitten (1982a) and McRae and Seinfeld (1983) mechanisms, shown in Tables 24-25, have not been modified to reflect the most recent determinations of the acetaldehyde quantum yields.

The Dodge mechanism (Table 26), which was based on the Schere and Demerjian (1977) photolysis rates, is similarly outdated. The photolysis rates in the Demerjian mechanism (Table 27), however, have been updated to reflect the recent quantum yield data obtained by Horowitz and Calvert (1982).

Penner and Walton (1982) employ an approach similar to Demerjian et al. (1980), see Table 28, and base their species data on: NO_2 -Hudson and Reed (1979), O_3 -Hudson and Reed (1979), H_2O_2 -Molina et al. (1977), NO_3 -Magnotta and Johnston (1980), N_2O_5 -Hudson and Reed (1979), HCHO -Bass et al. (1980), with quantum yields of Moortgat et al. (1980),

TABLE 24

Photolysis Reaction Steps in the Killus and Whitten (1982a)
Photochemical Reaction Mechanism^a

REACTION NUMBER	PHOTODISSOCIATION STEP ^(b)	PHOTOLYSIS RATE ^(c) RELATIVE TO NO ₂
1	NO ₂ + hv → NO + O(³ P)	1.0
37	CARB + hv → CO + H ₂	1.00x10 ⁻³
38	CARB + hv $\xrightarrow{O_2}$ 2/3(2HO ₂ + CO) +1/3(2MEO ₂ + CO + 2X)	2.00x10 ⁻³
67	DCRB + hv $\xrightarrow{O_2}$ 1/2(HO ₂ + ACO ₃ + CO) +1/2(MEO ₂ + HO ₂ + CO)	4.00x10 ⁻²
71 ^(d)	HONO + hv → OH + NO	1.80x10 ⁻¹
73	O ₃ + hv → O(¹ D)	1.00x10 ⁻³

Footnotes for Table 24

- (a) Mechanism documentation: Killus and Whitten (1982ab) and Whitten et al. (1980ab). There is little or no documentation of the sources used to establish the photolysis rate constants. In published applications of the mechanism, the rates appear to have been adjusted to match the experimental conditions.
- (b) CARB - Denotes carbonyl compounds such as aldehydes and ketones
DCRB - Highly photolytic alpha-dicarbonyl compounds
MEO₂ - Surrogate for alkylperoxyl radical
X₂ - Compound introduced to maintain carbon balance
- (c) The scaling ratios reported above are based on Table 3 of Killus and Whitten (1982a). The diurnal variations in photolysis rates, of most species, are based on the NO₂ value. The carbonyl (CARB) rates are determined from Demerjian et al. (1980) HCHO values using the formulae $k_{37} = 1/2 k(\text{HCHO} + hv \rightarrow \text{CO} + \text{H}_2)$ and $k_{38} = 2/3 k(\text{HCHO} + hv \rightarrow \text{HCO} + \text{H})$ (Killus, 1982a). Using Demerjian et al. (1980) $k_{37}/k_1 = k_{38}/k_1 = 2.8 \times 10^{-3}$.

TABLE 25

Photolysis Reaction Steps in the McRae and Seinfeld (1983)
Photochemical Reaction Mechanism^a

REACTION NUMBER	PHOTODISSOCIATION STEP ^(b)	PHOTOLYSIS RATE ^(c) RELATIVE TO NO ₂
1	NO ₂ + hv → NO + O(³ P)	1.00
10	HONO + hv → OH + NO	1.9x10 ⁻¹
20	O ₃ + hv → O(³ P) + O ₂	6.46x10 ⁻²
21	HCHO + hv → 2HO ₂ + CO	5.59x10 ⁻³
22	HCHO + hv → H ₂ + CO	9.31x10 ⁻³
25	RCHO + hv → RO ₂ + HO ₂ + CO	5.12x10 ⁻³
35 ^(d)	RONO + hv → NO + RO	2.20x10 ⁻¹
51	H ₂ O ₂ + hv → 2OH	3.17x10 ⁻³

Footnotes for Table 25

(a) Mechanism documentation: Falls and Seinfeld (1978), Falls et al. (1979), McRae et al. (1982ab) and McRae and Seinfeld (1983). The quantum yield and absorption cross sections used to calculate the photolysis rates are based on Schere and Demerjian (1977) and Demerjian et al. (1980).

(b) RCHO - Higher aldehydes
RONO - Alkyl nitrite
RO - Alkoxy radical
RO₂ - Alkylperoxy radical

(c) The rates have been scaled relative to the NO₂ photolysis step corresponding to a zenith angle z=0°. Diurnal variations are specified using the procedures described in either McRae et al. (1982b) or Demerjian et al. (1980).

(d) The RONO rate has been set to be 0.22 of the value for NO₂.

TABLE 26

Photolysis Reaction Steps in the Dodge (1977)
Photochemical Reaction Mechanism^a

REACTION NUMBER	PHOTODISSOCIATION STEP ^(b)	PHOTOLYSIS RATE ^(c) RELATIVE TO NO ₂
1	NO ₂ + hv → NO + O(³ P)	1.0
12	HONO + hv → OH + NO	5.62x10 ⁻²
17	H ₂ O ₂ + hv → 2OH	2.82x10 ⁻³
18	O ₃ + hv → O(¹ D)	7.28x10 ⁻³
19	O ₃ + hv → O(³ P)	5.72x10 ⁻²
49	HCHO + hv → Products	9.68x10 ⁻³
50	HCHO + hv → 2HO ₂	3.70x10 ⁻³
52	ALD2 + hv → Products	1.56x10 ⁻⁵
53	ALD2 + hv → MEO ₂ + HO ₂	7.35x10 ⁻⁴

Footnotes for Table 27

- (a) Mechanism Documentation: Dodge (1977). The absorption cross-section and quantum yield data used to develop the photolysis rates for this mechanism are based on the compilations of Schere and Demerjian (1977). The following photolysis reaction steps have fixed rate constants.

55	ALD3 + hv → Products	6.0x10 ⁻⁵	min ⁻¹
56	ALD3 + hv → C2O2 + HO2	2.5x10 ⁻³	min ⁻¹
58	ALD4 + hv → Products	6.0x10 ⁻⁵	min ⁻¹
59	ALD4 + hv → C3O2 + HO2	1.9x10 ⁻³	min ⁻¹

- (b) C2O2 - CH₃CH₂O₂
 C3O2 - CH₃CH₂CH₂O₂
 ALD2 - CH₃CHO
 ALD3 - CH₃CH₂CHO
 ALD4 - CH₃CH₂CH₂CHO

- (c) The photolysis rates have been scaled relative to the NO₂ value at a fixed zenith angle of z=0°.

TABLE 27

Photolysis Reaction Steps in the Demerjian (1982)
Photochemical Reaction Mechanism^a

REACTION NUMBER	PHOTODISSOCIATION STEP ^(b)	PHOTOLYSIS RATE ^(c) RELATIVE TO NO ₂
1	NO ₂ + hv → NO + O(³ P)	1.0
5	O ₃ + hv → O(¹ D) + O ₂	5.13x10 ⁻³
12	HONO + hv → OH + NO	1.80x10 ⁻¹
25	H ₂ O ₂ + hv → 2OH	1.01x10 ⁻³
30	HC ₃ + hv → 0.5RO ₂ + 1.5HO ₂ + CO	2.34x10 ⁻³
44	HC ₃ + hv → CO	2.81x10 ⁻³

Footnotes for Table 26

- (a) Mechanism documentation: Demerjian (1982) and Schere (1983). The absorption cross-sections and quantum yields for the species NO₂, O₃, HONO and H₂O₂ are based on the tabulations given in Demerjian et al. (1980). The photolysis rate constants for the aldehyde class (HC3) are based on a series of correction formulae developed by Schere (1983) to account for more recent quantum yield data obtained by Horowitz and Calvert (1982). The corrections are given by

$$\text{HC3} + \text{hv} \xrightarrow{30} k_{30} = 0.75 k(\text{A}) + 0.25 k(\text{C})$$

$$\text{HC3} + \text{hv} \xrightarrow{44} k_{44} = 0.75 k(\text{B})$$

where

$$\begin{aligned} k(\text{A}) &= 0.714 k(\text{HCHO} + \text{hv} \rightarrow \text{H} + \text{HCO}) \\ k(\text{B}) &= 0.676 k(\text{HCHO} + \text{hv} \rightarrow \text{H}_2 + \text{CO}) \\ k(\text{C}) &= 0.444 k(\text{CH}_3\text{CHO} + \text{hv} \rightarrow \text{CH}_3 + \text{HCO}) \quad (\text{Lower Limit}) \end{aligned}$$

The values for $k(\text{HCHO})$ and $k(\text{CH}_3\text{CHO})$ are from Demerjian et al. (1980).

- (b) HC₃ - Aldehydes
RO₂ - alkylperoxy radical
- (c) The photolysis rates have been scaled relative to the NO₂ value at a fixed zenith angle of $z=0^\circ$.

TABLE 28

Photolysis Reaction Steps in the Penner and Walton (1982)
Photochemical Reaction Mechanism^a

REACTION NUMBER	PHOTODISSOCIATION STEP ^(b)	PHOTOLYSIS RATE ^(c) RELATIVE TO NO ₂
J1	NO ₂ + hv → NO + O(³ P)	1.0
J2	O ₃ + hv → O(³ P) + O ₂	5.19x10 ⁻²
J3 ^(d)	O ₃ + hv → O ₂ + 2OH	4.74x10 ⁻⁴
J4	HONO + hv → OH + NO	2.26x10 ⁻¹
J5	H ₂ O ₂ + hv → 2OH	1.41x10 ⁻³
J6	NO ₃ + hv → NO ₂ + O(³ P)	1.56x10 ¹
J7	NO ₃ + hv → NO + O ₂	1.9
J8	N ₂ O ₅ + hv → NO ₂ + NO ₂ + O	4.64x10 ⁻⁶
J9 ^(e)	HC ₄ + hv → CO + H ₂	1.72x10 ⁻³
J10	HC ₄ + hv → CO + 2HO ₂	1.56x10 ⁻³
J11 ^(f)	HC ₄ + hv → CO + RO ₂ + HO ₂	1.56x10 ⁻³
J12 ^(g)	MGLY + hv → HO ₂ + RCO ₃ + CO	5.05x10 ⁻²

Footnotes for Table 28

- (a) Mechanism documentation: Gelinas and Skewes-Cox (1977), MacCracken and Sauter eds. (1975), Penner and Walton (1982) and Penner (1982). The absorption cross-section and quantum yield data used to calculate the photolysis rate are based on the values reported in the survey of Hudson and Reed (1979). The actinic irradiance values have been calculated using the model described in Luther and Gelinas (1976) using an assumption of 'clear' sky conditions. This results in higher NO₂ values than Demerjian et al. (1980). For example, the NO₂ rate corresponding to a zenith angle Z=0° is 0.694 min⁻¹. In atmospheric modeling applications this rate must be corrected for the presence of clouds and aerosols. In the application of the mechanism, the clear sky rate is multiplied by a cloud factor that usually ranges from 0.6 to 0.9. As such, it then describes photolysis in the middle of the one-layer model, e.g. about 200 m in San Francisco at mid-day.

Footnotes for Table 28 (Continued)

- (b) HC₄ - Aldehydes and ketones
M-GLY - Methylglyoxal (CH₃COCHO)
RO₂ - Alkylperoxy radical
RCO₃ - Peroxyacyl radical

- (c) The rates have been scaled relative to the NO₂ photolysis step at a zenith angle Z=0°. The variation of the photolysis rates for other zenith angles is given in Table 29

- (d) The photolysis rate J3 was determined by multiplying the photolysis rate for the reaction O₃ + hv → O(¹D) + O₂, shown in Table 29, by

$$\frac{[\text{H}_2\text{O}]}{[\text{M}]} \times \frac{2.3 \times 10^{-10}}{3.05 \times 10^{-11}}$$

- (e) The photolysis rates J9 and J10 for aldehydes and ketones (HC4) are equal to one half of the values for HCHO shown in Table 29.
- (f) The photolysis rate J11 is assumed to be 1/2 of the rate for the step HCHO + hv → HCO + H'
- (g) The methylglyoxal photolysis rate has been set to be 0.050 k(NO₂) on the basis of Darnall et al. (1979).

CH_3COCHO -5% of NO_2 rate and the actinic fluxes from Gelinas et al. (1974) and Luther and Gelinas (1976). Table 29 presents the zenith angle dependence of the photolysis rates used by Penner and Walton (1982).

A comparison of the photolysis rates used in each of the mechanisms is shown in Table 30. We note that even for common reactions, there are major differences in the rates. For further details about currently accepted values for σ_i and ϕ_i the reader is referred to the extensive evaluated reviews of Hudson and Reed (1979), Baulch et al. (1980,1982), WMO (1981), DeMore et al. (1982) and Atkinson and Lloyd (1983).

4.5 Uncertainty Estimates for the Photolysis Rates

There are two basic sources of uncertainty that arise during the calculation of photolysis rates needed for atmospheric modeling applications. One, which is common to all species and reaction mechanisms, is the specification of the actinic irradiance. Most of the mechanisms considered in this study establish the actinic flux from numerical solutions of mathematical models that describe the radiative transfer processes in the atmosphere. Many assumptions need to be made in order to specify the input data for these models including; the surface albedo and the the vertical distribution of aerosols and gases in the upper atmospheres. Depending on the choice of input data this can lead to a $\pm 20\%$ difference in the calculated fluxes. Similar levels of uncertainty are involved if the photolysis rates are based on ambient measurements of the ultraviolet flux.

TABLE 29

Calculated Ground Level Values of the Photolysis Rate Constants of Key Species as a Function of the Solar Zenith Angle for the Penner and Walton (1982) Photochemical Reaction Mechanism^a

ZENITH ANGLE	PHOTOLYSIS RATE CONSTANTS (min ⁻¹)(b)							
	NO ₂	HCHO→H	HCHO→H ₂	HONO	H ₂ O ₂	CH ₃ CHO	O ₃ →O(³ P)	O ₃ →O(¹ D)
0	0.694	2.16x10 ⁻³	2.38x10 ⁻³	0.157	9.82x10 ⁻⁴	2.16x10 ⁻³	3.60x10 ⁻²	3.67x10 ⁻³
10	0.687	2.14x10 ⁻³	2.36x10 ⁻³	0.155	9.70x10 ⁻⁴	2.12x10 ⁻³	3.58x10 ⁻²	3.54x10 ⁻³
20	0.665	1.98x10 ⁻³	2.24x10 ⁻³	0.151	9.18x10 ⁻⁴	1.98x10 ⁻³	3.50x10 ⁻²	2.53x10 ⁻³
30	0.625	1.76x10 ⁻³	2.04x10 ⁻³	0.140	8.22x10 ⁻⁴	1.76x10 ⁻³	3.32x10 ⁻²	2.52x10 ⁻³
40	0.567	1.46x10 ⁻³	1.78x10 ⁻³	0.127	7.08x10 ⁻⁴	1.46x10 ⁻³	3.10x10 ⁻²	1.80x10 ⁻³
50	0.493	1.11x10 ⁻³	1.45x10 ⁻³	0.110	5.64x10 ⁻⁴	1.11x10 ⁻³	2.84x10 ⁻²	1.09x10 ⁻³
60	0.395	7.20x10 ⁻⁴	1.05x10 ⁻³	0.087	3.98x10 ⁻⁴	7.20x10 ⁻⁴	2.49x10 ⁻²	4.92x10 ⁻⁴
70	0.270	3.48x10 ⁻⁴	6.02x10 ⁻⁴	0.057	2.22x10 ⁻⁴	3.58x10 ⁻⁴	2.04x10 ⁻²	1.26x10 ⁻⁴
78	0.143	1.23x10 ⁻⁴	2.62x10 ⁻⁴	0.029	9.40x10 ⁻⁵	1.23x10 ⁻⁴	1.56x10 ⁻²	2.45x10 ⁻⁵
86	0.033	1.86x10 ⁻⁵	5.48x10 ⁻⁵	0.007	1.84x10 ⁻⁵	1.86x10 ⁻⁵	6.06x10 ⁻³	3.42x10 ⁻⁶
90	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Footnotes for Table 29

(a) Material in this table has been derived from Penner (1983).

(b) The photolysis rates for NO₃ and Methylglyoxal are expressed as a fraction of the NO₂ rate as shown in Table 28.

TABLE 30

Comparison of Key Photolysis Steps Used In Different Photochemical
Reaction Mechanisms

PHOTOLYSIS STEP	PHOTOLYSIS RATE RELATIVE TO NO ₂ ^(a)					
	1	2	3	4	5	6
<u>NO₂ Normalized Photolysis Rates</u> ^(b)						
NO ₂ + hv → NO + O(³ P)	1.0	1.0	1.0	1.0	1.0	1.0
HONO + hv → OH + NO	0.17	0.18	0.056	0.18	0.19	0.23
HCHO + hv → CO + H ₂	0.0034	0.0038	0.0097	0.001	0.0093	0.0034
→ HCO [•] + H [•]	0.0035	0.0030	0.0037	0.002	0.0056	0.00312
CH ₃ CHO + hv → HCO [•] + CH ₃ [•]	0.0008	0.00036	0.0007	--	--	--
RCHO + hv → CO + a ₁ HO ₂ + a ₂ RO ₂	0.0008	0.0023	0.0025	--	0.0051	--

Footnotes for Table 30

(a) Reaction Mechanisms

- 1 Atkinson et al. (1982)
- 2 Demerjian (1982)
- 3 Dodge (1977)
- 4 Killus and Whitten (1982a)
- 5 McRae and Seinfeld (1983)
- 6 Penner and Walton (1982)

(b) The photolysis rates used by each mechanism have been normalized against the peak NO₂ values.

While the spectral distribution and intensity of the incident radiation are common to all the species, the efficiency with which light is absorbed depends on the properties of the molecule itself. Uncertainties associated with measurements of the species absorption cross-sections and quantum yields are the second major source of inaccuracy in the calculation of photolysis rates. Meaningful error assignment is a difficult problem partly because the measurement uncertainties tend to be random in nature. Table 31 gives the estimated reliability factors for some of the more important photochemical reactions. These factors represent the assessments by DeMore et al. (1982), Plum et al. (1983), Atkinson and Lloyd (1983) and WMO (1981) of the combined uncertainty in cross-sections and quantum yields. The tabulated values indicate, for example, that the product $\sigma\phi$ for NO_2 , over the wavelength band of interest, is uncertain to within one standard deviation by a factor of ± 1.2 . By combining this information with the errors involved in setting the actinic irradiance it is possible to set bounds for systematic sensitivity studies of the effects of photolytic processes on mechanism performance.

TABLE 31

Uncertainty Estimates for Photolysis Steps

PHOTOLYSIS STEP ^(a)	UNCERTAINTY ESTIMATE ^(b)
$\text{NO}_2 + \text{h}\nu \longrightarrow \text{NO} + \text{O}(^3\text{P})$	1.2
$\text{HONO} + \text{h}\nu \longrightarrow \text{OH} + \text{NO}$	1.4
$\text{H}_2\text{O}_2 + \text{h}\nu \longrightarrow 2\text{OH}$	1.4
$\text{NO}_3 + \text{h}\nu \longrightarrow \text{NO}_2 + \text{O}(^3\text{P})$	2.0
$\longrightarrow \text{NO} + \text{O}_2$	1.2
$\text{N}_2\text{O}_5 + \text{h}\nu \longrightarrow 2\text{NO}_2 + \text{O}$	2.0
$\text{O}_3 + \text{h}\nu \longrightarrow \text{O}_2 + \text{O}(^3\text{P})$	1.1
$\longrightarrow \text{O}(^1\text{D}) + \text{O}_2(^1\text{g})$	1.4
$\text{HCHO} + \text{h}\nu \longrightarrow \text{CO} + \text{H}_2$	1.4
$\longrightarrow \text{HCO} + \text{H}$	2.0
$\text{CH}_3\text{CHO} + \text{h}\nu \longrightarrow \text{CH}_4 + \text{CO}$	2.0
$\longrightarrow \text{HCO} + \text{CH}_3$	2.0
$\text{RCHO} + \text{h}\nu \longrightarrow \text{CO} + \text{a}_1\text{HO}_2 + \text{a}_2\text{RO}_2$	2.0
$\text{GLY} + \text{h}\nu \longrightarrow \text{HCHO} + \text{CO}$	2.0
$\text{M-GLY} + \text{h}\nu \longrightarrow \text{HO}_2 + \text{RCO}_3 + \text{CO}$	2.0
$\text{MEK} + \text{h}\nu \longrightarrow \text{CH}_3\text{CO}_3 + \text{C}_2\text{H}_5\text{O}_2$	2.0

Footnotes for Table 31

(a) Mechanism steps as defined in Table 20

(b) Based on Atkinson and Lloyd (1983), WMO (1981) and DeMore et al. (1982)

CHAPTER 5

SPECIFICATION OF INITIAL CONDITIONS AND REACTION RATE CONSTANTS FOR LUMPED ORGANIC REACTIONS

Each mechanism considered in this study employs a different method for partitioning individual organics into the appropriate lumped classes. The primary purpose of this chapter is to document these procedures and the methods used to establish initial conditions and lumped rate constants. Two basic questions are addressed. The first is given a set of detailed hydrocarbon measurements how should the individual species be allocated to the lumped classes. A more difficult problem, and one that is frequently encountered in practice, is how to establish initial concentrations for the lumped classes when only total or non-methane hydrocarbon measurements are available.

5.1 Species Assignment to Lumped Hydrocarbon Classes

As noted previously in Chapter 1, the six reaction schemes considered in this study use one of three basic approaches to hydrocarbon lumping. With the exception of those mechanisms employing surrogate species most of the other lumping schemes utilize an organic classification scheme that is based on either the molecule type or carbon bond structure. A summary of these approaches is presented in Table 32. Formal definitions of the compositions of the lumped classes used in each mechanism are presented in Tables 33-38.

Table 39 shows how the initial concentrations in smog chamber experiment SUR-119J are classified for the five mechanisms. This particular chamber run was carried out at the University of California, Riverside (Pitts et al. 1976) and was simulated in this study to test the

TABLE 32

Number of Organic Classes and Lumping Procedures
Used in the Reaction Mechanism Survey

REACTION MECHANISM DOCUMENTATION	NUMBER OF REACTIVE ORGANIC GROUPINGS ^(a)	APPROACH TO ORGANIC LUMPING
1 Atkinson et al. (1979,1982) Carter et al. (1979) Lurmann (1982,1983)	14	Grouping by molecule type with surrogate species for particular classes
2 Demerjian (1982) Schere (1983)	4	Grouping by molecule type
3 Dodge (1977) Durbin et al. (1975)	4	Chemistry represented by a surrogate mixture of propene and butane
4 Killus and Whitten (1982a,b) Whitten et al. (1980a,b)	5	Species grouping on the basis of bond structure
5 McRae and Seinfeld (1983) McRae et al. (1982) Falls et al. (1979) Falls and Seinfeld (1978)	6	Grouping by molecule type
6 Penner and Walton (1982) MacCracken and Sauter (1975) Gelinas and Skewes-Cox (1975)	4	Grouping by molecule type

Footnotes for Table 32

(a) The detailed class definition are contained in the following

- 1 Atkinson et al. (1982) - Table 33
- 2 Demerjian (1982) - Table 34
- 3 Dodge (1977) - Table 35
- 4 Killus and Whitten (1982) - Table 36
- 5 McRae and Seinfeld (1983) - Table 37
- 6 Penner and Walton (1982) - Table 38

TABLE 32

Number of Organic Classes and Lumping Procedures
Used in the Reaction Mechanism Survey

REACTION MECHANISM DOCUMENTATION	NUMBER OF REACTIVE ORGANIC GROUPINGS ^(a)	APPROACH TO ORGANIC LUMPING
1 Atkinson et al. (1979,1982) Carter et al. (1979) Lurmann (1982,1983)	14	Grouping by molecule type with surrogate species for particular classes
2 Demerjian (1982) Schere (1983)	4	Grouping by molecule type
3 Dodge (1977) Durbin et al. (1975)	4	Chemistry represented by a surrogate mixture of propene and butane
4 Killus and Whitten (1982a,b) Whitten et al. (1980a,b)	5	Species grouping on the basis of bond structure
5 McRae and Seinfeld (1983) McRae et al. (1982) Falls et al. (1979) Falls and Seinfeld (1978)	6	Grouping by molecule type
6 Penner and Walton (1982) MacCracken and Sauter (1975) Gelinas and Skewes-Cox (1975)	4	Grouping by molecule type

Footnotes for Table 32

(a) The detailed class definition are contained in the following

- 1 Atkinson et al. (1982) - Table 33
- 2 Demerjian (1982) - Table 34
- 3 Dodge (1977) - Table 35
- 4 Killus and Whitten (1982) - Table 36
- 5 McRae and Seinfeld (1983) - Table 37
- 6 Penner and Walton (1982) - Table 38

TABLE 33

Definition of Organic Classes in the Atkinson et al. (1982)
Photochemical Reaction Mechanism^a

ORGANIC CLASS	DEFINITION OF THE ORGANIC CLASS	COMPUTER CODE ^b
Alkanes	Propane (excluding CH ₄ and C ₂ H ₆)	PRPA
	Alkanes with carbon number ≥ 4	ALKA
Alkenes	Ethylene	ETHE
	Propene is the surrogate species for the 1-alkenes	PRPE
	Trans-2-butene is the surrogate species for the internal alkenes	BUTE
Aromatics	Benzene	BENZ
	Toluene is the surrogate species for the monoalkylbenzenes	TOLU
	Xylene is the surrogate species for the di- and tri-alkylbenzenes	XYEN
Carbonyls	Formaldehyde	HCHO
	Acetaldehyde	ALD2
	Benzaldehyde	ACHO
	Propionaldehyde is the surrogate species for the higher aldehydes	RCHO
	Acetone	ACET
	Methylethylketone is the surrogate for higher ketones	MEK
Unreactive		UR

Footnotes for Table 33:

(a) Mechanism documentation: Atkinson et al.(1979,1982), Carter et al.(1979)

(b) The computer codes correspond to those used in Chapter 1

TABLE 34

Definition of Organic Classes in the Demerjian (1982)
Photochemical Reaction Mechanism^a

ORGANIC CLASS	DEFINITION OF THE ORGANIC CLASS	COMPUTER CODE ^b
Alkenes	All alkenes including ethylene	HC1
Alkanes	All alkanes other than methane	HC2
Aldehydes	All aldehyde species	HC3
Aromatics	All aromatic species	HC4
Unreactive		UR

Footnotes for Table 34:

- (a) Mechanism documentation: Demerjian (1982), Schere (1983)
(b) The computer codes correspond to those used in Chapter 1

TABLE 35

Definition of Organic Classes in the Dodge (1977)
Photochemical Reaction Mechanism^a

ORGANIC CLASS	DEFINITION OF THE ORGANIC CLASS	COMPUTER CODE ^b
Alkenes	Propylene	PROP
Alkanes	Butane	BUT
Aldehydes	Formaldehyde	HCHO
	Acetaldehyde (CH_3CHO)	ALD2
Unreactive		UR

Footnotes for Table 35:

(a) Mechanism Documentation: Dodge (1977)

(b) The computer codes correspond to those used in Chapter 1.

TABLE 36

Definition of Organic Classes in the Killus and Whitten (1982a)
Photochemical Reaction Mechanism^a

ORGANIC CLASS	DEFINITION OF THE ORGANIC CLASS	CARBON NUMBER	COMPUTER CODE ^b
Olefins	1-alkene carbon atoms except ethene	2	OLE
	Ethene	2	ETH
Paraffins	Single-bonded carbon atoms	1	PAR
Aromatics	Reactive aromatic rings	6	ARO
Carbonyls	Carbonyl carbon atoms plus the carbon atoms from internal olefins	1	CARB
Unreactive		-	UR

Footnotes for Table 36:

(a) Mechanism documentation: Killus and Whitten (1982a)
Whitten et al. (1980a,b)

(b) The computer codes correspond to those used in Chapter 1

TABLE 37

Definition of Organic Classes in the McRae and Seinfeld (1983)
Photochemical Reaction Mechanism^a

ORGANIC CLASS	DEFINITION OF THE ORGANIC CLASS	COMPUTER CODE ^b
Aldehydes	Formaldehyde	HCHO
	Higher aldehydes	RCHO
Aromatics	All aromatics	ARO
Alkenes	Ethene	C2H4
	All olefins except ethene	OLE
Alkanes	All alkanes except methane	ALK
Unreactive		UR

Footnotes for Table 37:

(a) Mechanism documentation: Falls and Seinfeld (1978), Falls et al. (1979)
McRae et al. (1981), McRae and Seinfeld (1982)

(b) The computer codes correspond to those used in Chapter 1

TABLE 38

Definition of Organic Classes in the Penner and Walton (1982)
Photochemical Reaction Mechanism^a

ORGANIC CLASS	DEFINITION OF THE ORGANIC CLASS	COMPUTER CODE ^b
Alkenes	Includes all alkenes, isoprene and mono-terpenes. The reaction rate constants are based on propylene.	HC1
Alkanes	Includes all alkanes. The reaction rate constants are based on n-butane.	HC2
Aromatics	Includes all aromatics. The reaction rate constants are based on toluene.	HC3
Carbonyls	Includes all aldehydes and ketones. The rate constants are based on a mixture 50%-50% mixture of HCHO and CH ₃ CHO.	HC4
Unreactive		UR

Footnotes for Table 38:

(a) Mechanism documentation: Gelinas and Skewes-Cox (1977)
MacCracken and Sauter eds. (1975)
Penner and Walton (1982)
Penner (1982)

(b) The computer codes correspond to those used in Chapter 1

TABLE 39

Classification of Organic Species into Lumped Classes
for the Smog Chamber Experiment SUR-119J^(a)

SPECIES	CONCENTRATION		SPECIES ASSIGNMENT FOR EACH MECHANISM					
	ppbV	ppbC	1	2	4	5	6 ^(b)	
Methane (CH ₄)	2740.0	2740.0	UR	UR	1UR	UR	UR	
Acetylene (C ₂ H ₂)	46.4	92.8	UR	UR	1UR	UR	UR	
Ethane (C ₂ H ₆)	76.8	153.6	UR	HC2	2UR	ALK	HC2	
Propane (C ₃ H ₈)	17.0	51.0	PRPA	HC2	1.5PAR+1.5UR	ALK	HC2	
Acetone (CH ₃ COCH ₃)	35.2	105.6	ACET	UR	2PAR+1CARB	UR	HC4	
Isobutane (C ₄ H ₁₀)	0.2	0.8	ALKA	HC2	4PAR	ALK	HC2	
n-Butane	166	664	ALKA	HC2	4PAR	ALK	HC2	
2,3-Dimethyl Butane (C ₄ H ₈ -(CH ₃) ₂)	97.6	585.6	ALKA	HC2	6PAR	ALK	HC2	
Ethene (C ₂ H ₄)	43.2	86.4	ETHE	HC1	1ETH	C2H4	HC1	
Propene (C ₃ H ₆)	10.6	31.8	PRPE	HC1	1OLE+1PAR	OLE	HC1	
Trans-2-Butene (C ₄ H ₈)	0.7	2.8	BUTE	HC1	2PAR+2CARB	OLE	HC1	
Cis-2-Butene (C ₄ H ₈)	13.0	52.0	BUTE	HC1	2PAR+2CARB	OLE	HC1	
2-methyl-2-Butene (C ₄ H ₇ -CH ₃)	14.8	74.0	BUTE	HC1	3PAR+2CARB	OLE	HC1	
Benzene (C ₆ H ₆)	1.6	9.6	BENZ	HC4	6UR	ARO	HC3	
Toluene (C ₆ H ₅ -CH ₃)	16.8	117.6	TOLU	HC4	1PAR+1ARO	ARO	HC3	
Ethyl Benzene (C ₆ H ₅ -C ₂ H ₅)	6.4	51.2	TOLU	HC4	2PAR+1ARO	ARO	HC3	
Meta-xylene (C ₆ H ₄ -(CH ₃) ₂)	42.4	339.2	XYEN	HC4	2PAR+1ARO	ARO	HC3	
Isopropyl Benzene (C ₆ H ₅ -C ₃ H ₇)	0.4	3.6	TOLU	HC4	3PAR+1ARO	ARO	HC3	
n-Propyl Benzene ((C ₆ H ₄ -C ₃ H ₇) _n)	0.1	0.9	TOLU	HC4	3PAR+1ARO	ARO	HC3	
Meta-Ethyl Toluene (C ₆ H ₄ -CH ₃ -C ₂ H ₅)	1.0	9.0	XYEN	HC4	3PAR+1ARO	ARO	HC3	
1,2,3 Trimethyl Benzene (C ₆ H ₃ -(CH ₃) ₃)	1.6	14.4	XYEN	HC4	3PAR+1ARO	ARO	HC3	

TABLE 39 (Continued)

SPECIES	CONCENTRATION		SPECIES ASSIGNMENT FOR EACH MECHANISM				
	ppbV	ppbC	1	2	4	5	6 ^(b)
Formaldehyde (HCHO)	38.0	38.0	HCHO	HC3	1CARB	HCHO	HC4
Acetaldehyde (CH ₃ CHO)	20.0	40.0	ALD2	HC3	1PAR+1CARB	RCHO	HC4
Propionaldehyde (C ₂ H ₅ CHO)	3.2	9.6	RCHO	HC3	2PAR+1CARB	RCHO	HC4
Nitric Oxide (NO)	301.0						
Nitrogen Dioxide (NO ₂)	41.0						
Nitrous Acid (HONO)	12.0						
Carbon Monoxide (CO)	7450.0						
Water (H ₂ O) (ppm)	15500.0						
Oxygen (O ₂) (ppm)	210,000.0						
M (ppm)	1,000,000.0						
<u>TOTALS FOR MIXTURE</u>							
Nitrogen oxides (ppbV)	354.0						
THC (ppbV)	3393.0						
THC (ppbC)	5274.0						

Footnotes for Table 39:

- (a) The initial conditions correspond to smog chamber experiment SUR-119J carried out at the University of California Riverside. The additional data needed to characterize the experimental conditions are (Pitts et al. 1976):

Dilution Rate = $3.5 \times 10^{-4} \text{ min}^{-1}$
 Chamber temperature = $303.5 - 306.1^\circ \text{K}$
 Relative humidity = $58.5 - 53.0\%$
 Photolysis Rate k_1 = 0.31 min^{-1}

- (b) Some "unreactive" species are included in Penner and Walton (1982) but with low reactivity coefficients.⁻³ For example, the reactivity of methane relative to HC2 is 3.6×10^{-3} .

various mechanisms.

The first step in the assignment process for any mechanism is to classify each species into its appropriate lumped class. For example, 1,2,3-trimethylbenzene is an aromatic compound and is assigned to the following lumped classes.

Mechanism	Class Assignment
Atkinson et al. (1982)	XYEN
Demerjian (1983)	HC4
Killus and Whitten (1982a)	3 PAR + 1 ARO
McRae and Seinfeld (1983)	ARO
Penner and Walton (1982)	HC3

The process is repeated for each species to calculate the molar concentration of each lumped class. The results of these calculations together with the determinations of the average carbon numbers for smog chamber experiment SUR-119J are shown in Table 40.

In the mechanism of Killus and Whitten (1982a) the molecular bond is used as a basic unit rather than the molecule itself. To illustrate how the initial apportionment is carried out, consider the two compounds, propene and cis-2-butene, shown in Figure 11. On the basis of the above class definitions, propene, is equivalent to 1 PAR + 1 OLE and cis-2-butene is composed of 2 PAR and 1 OLE. While this assignment process is straightforward, there are some important exceptions to it. In Figure 11 cis-2-butene is shown to be equivalent to 2 PAR + 1 OLE, however Killus and Whitten (1982a) recommend that the molecule be split into 2 PAR and 2 CARB. The reason for this is that internal alkenes react more rapidly than do terminal alkenes like propene. In order to eliminate intermediate species that have very short lifetimes, Killus

TABLE 40

Summary of the Concentrations in Each Lumped Class
for the Smog Chamber Experiment SUR-119J

CODE		ppbV	ppbC	C#
Atkinson et al. (1982)				
1	PRPA	17.00	51.00	3.00
2	ALKA	263.80	1250.40	4.74
3	ETHE	43.20	86.40	2.00
4	PRPE	10.60	31.80	3.00
5	BUTE	28.50	128.80	4.52
6	BENZ	1.60	9.60	6.00
7	TOLU	23.70	173.30	7.31
8	XYEN	45.00	362.60	8.06
9	HCHO	38.00	38.00	1.00
10	ALD2	20.00	40.00	2.00
12	RCHO	3.20	9.60	3.00
13	ACET	35.20	105.60	3.00
15	UR	2863.20	2986.40	1.04
Demerjian (1982)				
1	HC1	82.30	247.00	3.00
2	HC2	357.60	1455.00	4.07
3	HC3	61.20	87.60	1.43
4	HC4	70.30	545.50	7.76
5	UR	2821.60	2938.40	1.04
Killus and Whitten (1982a)				
1	OLE	10.60	21.20	2.00
2	PAR	1578.80	1578.80	1.00
3	ARO	68.70	412.20	6.00
4	CARB	153.40	153.40	1.00
5	ETH	43.20	86.40	2.00
6	UR	2975.10	3021.50	1.02

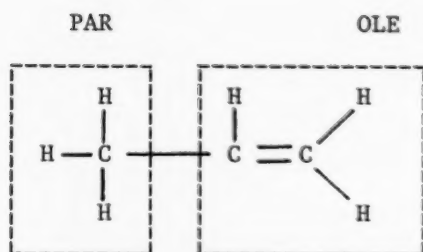
TABLE 40 (Continued)

CODE		ppbV	ppbC	C#
McRae and Seinfeld (1983)				
1	HCHO	38.00	38.00	1.00
2	RCHO	23.20	49.60	2.14
3	ARO	70.30	545.50	7.76
4	C2H4	43.20	86.40	2.00
5	OLE	39.10	160.60	4.11
6	ALK	357.60	1455.00	4.07
7	UR	2821.60	2938.40	1.04
Penner and Walton (1982)				
1	HC1	82.30	247.00	3.00
2	HC2	357.60	1455.00	4.07
3	HC3	70.30	545.50	7.76
4	HC4	96.40	193.20	2.00
5	UR ^(a)	2786.40	2832.80	1.02

Footnote for Table 40

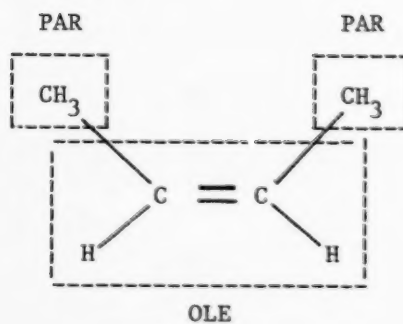
- (a) In the Penner and Walton (1982) mechanism, these species are actually included in HC2 but their reactivity weights are extremely low and, hence, these species can be considered to be unreactive.

Propylene (Propene) 1 OLE + 1 PAR



(a)

Cis-2-Butene 1 OLE + 2 PAR



(b)

FIGURE 11
Classification of (a) Propylene and
(b) Cis-2-Butene into the Carbon-Bond Categories

and Whitten treat internal alkenes as if they had already reacted. Thus, cis-2-butene is classified as being equivalent to 2 PAR + 2 CARB. In passing it is interesting to note that the use of this approximation ignores one NO to NO₂ conversion by the peroxy radical formed from the initial OH attack (See Figure 7).^{*} Cycloparaffins are another case where the simple carbon bond class definitions are insufficient. For these compounds, Killus and Whitten (1982a) assume that at some point in the reaction scheme the ring structure must break, yielding two reactive sites instead of one. To account for this property a CARB group is added to the split for the paraffin group. For example cyclopentane (C₅H₁₀) is decomposed into 4 PAR + 1 CARB. Killus and Whitten have classified over 200 compounds into their carbon bond classes providing guidance as to how an individual organic should be apportioned.

5.2 Calculation of Lumped Reaction Rate Constants

Once the methodology for assigning individual species to each lumped organic class has been defined, then the only remaining information needed to specify the reaction kinetics is the corresponding lumped rate constants.

Five basic methods for specifying the needed rate constants have been developed:

^{*} The loss of an NO to NO₂ conversion is approximately compensated by the elimination of the ozone loss to the ozone-alkene reaction that would have occurred in the mechanism if the alkene were not treated as having already reacted.

- (1) the use of surrogate species rate constants (Dodge, 1977)
- (2) the use of surrogate species rate constants for particular lumped classes (Atkinson et al., 1982)
- (3) the use of mole-weighted lumped rate constants based on initial concentrations (Demerjian, 1982; McRae and Seinfeld, 1983)
- (4) the use of reactivity-weighted lumped rate constants (Penner and Walton, 1982)
- (5) the use of fixed rate constant values based on the reactions of particular carbon bond types (Killus and Whitten, 1982a)

When the mixture chemistry is represented by a set of surrogate species that have known rate constants, e.g. Dodge (1977) and Atkinson et al. (1982), the lumping problem is embodied in that of determining the proper initial conditions for the surrogate species. As an illustration of the effect of the selection of species to be used as surrogates for specifying lumped rate constants, consider the reactions of the hydroxyl radical and those alkene species that comprise the internal alkene class (BUTE) used in the Atkinson et al. (1982) mechanism. For the reactions of cis-2-butene and trans-2-butene the arithmetic average rate constant for the BUTE + OH $\rightarrow$ reaction is 9.14×10^4 , whereas the surrogate rate constant, which for Atkinson et al. (1982) is based on trans-2-butene, is 10.3×10^4 . Thus, the use of this surrogate rate constant may lead to an overestimate of the reaction rate for the lumped class depending on the distribution of species comprising that class. Note that in the surrogate species approach the surrogate rate constant does not reflect the initial conditions of the mixture. For example, in smog chamber experiment SUR-119J, the species distribution of the cis-2-butene (13.0 ppb) and trans-2-butene (0.7 ppb) that comprise the lumped class is not reflected in the rate constant value.

One way of accounting for the differences in composition and chemical reactivity of the species comprising each lumped class is to use a weighting scheme for lumped rate constants based on the initial molar concentrations of the species. This formulation, which is used by Demerjian (1982) and McRae and Seinfeld (1983), provides a simple way of incorporating the contribution of individual species to the reactivity of the mixture as a whole. In particular, it ensures that the lumped rate constant is not dominated by those species that may have large rate constants but only small initial concentrations. As an illustration of this point, the mole-weighted OH rate constant, corresponding to the conditions of experiment SUR-119J, is $8.09 \times 10^4 \text{ ppm}^{-1} \text{ min}^{-1}$. This value reflects the fact that the most of the initial mixture is composed of cis-2-butene. Practical applications of the mole-weighting scheme are considerably simplified because of the availability of extensive literature compilations of basic species rate constant data, e.g. Hampson and Garvin (1978), Atkinson et al. (1979), Baulch et al. (1980, 1982), Demore et al. (1982), and Atkinson and Lloyd (1983). A shortcoming of this approach is that, as the mixture reacts, the molar distribution changes, and this change is not reflected in the rate constants which were set based on the initial concentrations.

Penner and Walton (1982) use reactivity weighting of initial conditions so that the lumped reaction rate matches the rate based on the individual species in each class as explained by Gelinas and Skewes-Cox (1977).

In the carbon-bond mechanism the carbon bond, rather than the molecule itself, is used as the basic unit in each reaction step. It

is assumed that: (1) the reactions of each carbon atom (or double bond) are independent of the reactions elsewhere in the molecule and (2) carbon atoms with similar bonding react at similar rates (Whitten et al. 1980). Greiner (1970), for example, has shown that the total rate of H-atom abstraction by OH attack on an alkane molecule can be predicted from a knowledge of the molecule structure defined in terms of the number of primary, secondary or tertiary carbon atoms. Using this idea Whitten et al. (1980) established a suggested, or default, value for the rate constant for the reaction between the singly bonded alkane group PAR and the hydroxyl radical. The default value of $1300 \text{ ppmC}^{-1} \text{ min}^{-1}$, expressed on a per carbon atom basis, is within 35% of the OH rates of alkanes that are likely to be encountered in atmospheric modeling applications.

Documentation of the carbon bond mechanism (Killus and Whitten, 1982a) indicates that the use of default carbon bond rate constants can provide quite accurate simulations of several urban mixes. Nevertheless, Killus and Whitten have provided potential users of the mechanism documentation (Whitten et al., 1979) for modifying the carbon bond rate constants for special cases outside the range of urban mixes considered. In such cases, the weighted RMS average is recommended for the actual molecules to be simulated. For example, the current default rate constant for aromatics chemistry is based on a 50/50 mix of toluene and m-xylene; if the potential simulation involves exclusively xylenes, then the OH-rate constant should be increased to the weighted RMS value and the secondary chemistry should be modified to reflect the

known differences between mono (toluene) and the more substituted benzenes.

One of the advantages of the carbon bond approach is that the use of default values for each carbon-bond category reduces the range of rate constants that must be averaged in forming condensed reaction steps. Consider specifying the OH + PAR rate constant for the smog chamber experiment EC-231. The alkanes, n-butane (4 PAR) and 2,3-dimethylbutane (6 PAR) have OH rate constants of approximately 3,828 and 8,380 $\text{ppm}^{-1}\text{-min}^{-1}$ (Atkinson et al. 1979). If these rates are grouped by the numbers of single-bonded carbon atoms these rates become 957 and 1396 $\text{ppmC}^{-1}\text{-min}^{-1}$. Even though the rate constant range has been reduced the net reaction rate of the two species is unchanged. While the per carbon atom default rate constant is lower than the equivalent mole-weighted rate, the concentrations of the species comprising the lumped class are much higher because they are expressed on a carbon basis. As a result the combination of a reduced rate constant and higher initial conditions leads to no change in the range of the rates contributing to the PAR kinetics.

5.3 Atmospheric Modeling Applications

Over the past decade there have been significant improvements in the knowledge of the chemistry of polluted atmospheres. From a practical point of view the usefulness of these advances has, to a certain extent, been negated by the lack of similar developments in the collection and analysis of air quality and emissions data. For example at present the only data on ambient hydrocarbon levels, that are available

on a routine basis, are measurements of total, and in some cases, non-methane hydrocarbons. Given this highly aggregated information it can be expected that the process of establishing the appropriate initial conditions, for atmospheric modeling applications, can lead to a great deal of uncertainty.

Before discussing the different approaches that can be used to set the initial conditions in atmospheric applications it is useful to describe some of the limitations imposed by the use of routine monitoring data. Stephens and Hellrich (1980) discuss some of the errors involved in trying to establish just the non-methane (NMHC) fraction from the total hydrocarbon data collected by air pollution control agencies. If the flame ionization detectors are not accurately calibrated for both methane and THC it is possible to generate negative NMHC values! This is just one illustration, for further details about experimental techniques and the effects of interferences the reader is referred to Leinster et al. (1977), Lamb et al. (1980) and Simoneit and Mazurek (1981). We now describe some of the methods that can be used to set initial conditions when only highly aggregated data are available.

Despite the inherent limitations of the routine monitoring data there are, nevertheless, several methods that can be used to estimate the needed composition information. One of the most commonly employed techniques is to apportion the ambient hydrocarbon measurements into the appropriate lumped classes by using splitting factors derived from detailed gas chromatographic studies. For example, the published

results of Altshuller et al. (1963,1971), Calvert (1976), Jettes and Burghardt (1972), Kopczynski et al. (1972,1975), Lonneman et al. (1974,1978), Neligan (1962), Pitts et al. (1976) and Stephens and Burleson (1969) serve as an information base for establishing typical hydrocarbon levels in urban areas. Detailed reviews of these and other measurement programs can be found in; Graedel (1978), Killus and Whitten (1982a), Leinster et al. (1977), Lamb et al. (1980) and Simoneit and Mazurek (1981). Table 41 presents a typical composition profile for Los Angeles that was derived by combining the measurements made by Calvert (1976) with carbonyl data from Pitts et al. (1976). Given such a profile the splitting factors for each mechanism can be calculated by applying the procedures described in the footnotes of Table 42.

Once the splitting factors have been developed they then provide a means for allocating ambient measurements of either total or non-methane hydrocarbons to the appropriate lumped class used by each mechanism. A summary of the results from one set of calculations is shown in Table 42. While the above procedures are quite simple to use, some uncertainties can arise in atmospheric modeling applications. Such factors as the location of the area, the availability of gas chromatograph measurements and the judgement of the investigator can influence the selection of a 'typical' composition profile. Some indication of the effect of these differences can be seen in Table 43 where the urban splitting factors, recommended by the developer of each reaction mechanism, have been compared with splitting factors based on Table 42. The differences are particularly high for those lumped classes that

TABLE 41

Classification of Hydrocarbon Species into Lumped Classes
for a Typical Urban Composition Profile

HYDROCARBON SPECIES	ppbV	SPECIES ASSIGNMENT FOR EACH MECHANISM ^(a)						^(b)
		1	2	4	5	6		
1 1-heptene	4.4	PRPE	HC1	1 OLE	+ 5 PAR	OLE		HC1
2 1-hexene	1.7	PRPE	HC1	1 OLE	+ 4 PAR	OLE		HC1
3 1-pentene	4.0	PRPE	HC1	1 OLE	+ 3 PAR	OLE		HC1
4 2.2.4-trimethylpentane	2.5	ALKA	HC2	8 PAR		ALK		HC2
5 2.2.3-trimethylbutane	7.7	ALKA	HC2	7 PAR		ALK		HC2
6 2.2.5-trimethylhexane	1.0	ALKA	HC2	9 PAR		ALK		HC2
7 2.3.3-trimethylpentane	1.9	ALKA	HC2	8 PAR		ALK		HC2
8 2.2-dimethyl-1-butene	0.8	PRPE	HC1	4 PAR	+ 2 CARB	OLE		HC1
9 2-methyl pentane	11.0	ALKA	HC2	6 PAR		ALK		HC2
10 2-methyl-2-butene	0.8	BUTE	HC1	3 PAR	+ 2 CARB	OLE		HC1
11 2-methylhexane	6.9	ALKA	HC2	7 PAR		ALK		HC2
12 3-methyl pentane	10.0	ALKA	HC2	6 PAR		ALK		HC2
13 3-methyl hexane	6.3	ALKA	HC2	7 PAR		ALK		HC2
14 Acetaldehyde	20.0	ALD2	HC3	1 PAR	+ 1 CARB	RCHO		HC4
15 Acetylene	38.0	UR	UR	1 UR		UR		UR
16 Benzene	8.2	BENZ	HC4	6 UR		ARO		HC3
17 1-butene	1.5	PRPE	HC1	1 OLE	+ 2 PAR	OLE		HC1
18 Cyclohexene	10.7	BUTE	HC1	4 PAR	+ 2 CARB	OLE		HC1
19 Cyclopentane	2.6	ALKA	HC2	4 PAR	+ 1 CARB	ALK		HC2
20 Ethane	49.0	UR	HC2	2 UR		ALK		HC2
21 Ethylbenzene	4.1	TOLU	HC4	2 PAR	+ 1 ARO	ARO		HC3
22 Ethylene	43.0	ETHE	HC1	1 ETH		C2H4		HC1
23 Formaldehyde	38.8	HCHO	HC3	1 CARB		HCHO		HC4
24 Heptane	4.3	ALKA	HC2	7 PAR		ALK		HC2
25 Hexane	10.0	ALKA	HC2	6 PAR		ALK		HC2
26 Iso-butane	12.0	ALKA	HC2	4 PAR		ALK		HC2
27 Iso-pentane	44.3	ALKA	HC2	5 PAR		ALK		HC2
28 Isobutylene	3.0	PRPE	HC1	1 OLE	+ 2 PAR	OLE		HC1
29 Methane	2010.0	UR	UR	1 UR		UR		UR
30 Methylcyclohexane	3.7	ALKA	HC2	6 PAR	+ 1 CARB	ALK		HC2
31 Methylcyclohexene	4.7	BUTE	HC1	5 PAR	+ 2 CARB	OLE		HC1
32 Nonane	1.3	ALKA	HC2	9 PAR		ALK		HC2
33 Octane	2.1	ALKA	HC2	8 PAR		ALK		HC2
34 Propane	37.0	PRPA	HC2	1.5 PAR	+ 1.5 UR	ALK		HC2
35 Propionaldehyde	6.4	RCHO	HC3	2 PAR	+ 1 CARB	RCHO		HC4
36 Propylene	8.7	PRPE	HC1	1 OLE	+ 1 PAR	OLE		HC1
37 Sec-butylbenzene	5.0	TOLU	HC4	4 PAR	+ 1 ARO	ARO		HC3

TABLE 41 (Continued)

Classification of Hydrocarbon Species into Lumped Classes
for a Typical Urban Composition Profile

HYDROCARBON SPECIES	ppbV	SPECIES ASSIGNMENT FOR EACH MECHANISM ^(a)					
		1	2	4	5	6	
38 Toluene	20.0	TOLU	HC4	1 PAR + 1 ARO	ARO	HC3	
39 Undecane	1.0	ALKA	HC2	11 PAR	ALK	HC2	
40 n-butane	37.0	ALKA	HC2	4 PAR	ALK	HC2	
41 n-decane	1.1	ALKA	HC2	10 PAR	ALK	HC2	
42 n-dodecane	3.0	ALKA	HC2	12 PAR	ALK	HC2	
43 n-pentane	16.2	ALKA	HC2	5 PAR	ALK	HC2	
44 n-propylbenzene	1.0	TOLU	HC4	3 PAR + 1 ARO	ARO	HC3	
45 o-xylene	6.0	XYEN	HC4	2 PAR + 1 ARO	ARO	HC3	
46 p-xylene	14.0	XYEN	HC4	2 PAR + 1 ARO	ARO	HC3	
Totals	2526.7						

Footnotes for Table 41

- (a) The codes used for each reaction mechanism are defined in the following tables

- 1 Atkinson et al. (1982)
- 2 Demerjian (1982)
- 4 Killus and Whitten (1982a)
- 5 McRae and Seinfeld (1983)
- 6 Penner and Walton (1982)

- (b) The Penner and Walton (1982) mechanism uses reactivity weighting when individual hydrocarbons are grouped into the lumped classes. For example, 1 ppm of ethene is represented as 0.5 ppm of HCl in order to account for the lower reactivity of ethene relative to propene. Thus, for the PW mechanism the lumped classes shown in this table represent only the class into which each hydrocarbon is grouped.

TABLE 42

Summary of the Concentrations in Each Lumped Classes
for a Typical Urban Composition Profile

CODE	ppbV	ppbC	C#	THC SPLIT ^a	RHC SPLIT ^b
Atkinson et al. (1982)					
1 PRPA	37.00	111.00	3.00	0.0089	0.0187
2 ALKA	185.90	1030.50	5.54	0.0447	0.0940
3 ETHE	43.00	86.00	2.00	0.0103	0.0217
4 PRPE	24.10	109.90	4.56	0.0058	0.0122
5 BUTE	16.20	101.10	6.24	0.0039	0.0082
6 BENZ	8.20	49.20	6.00	0.0020	0.0041
7 TOLU	30.10	231.80	7.70	0.0072	0.0152
8 XYEN	20.00	160.00	8.00	0.0048	0.0101
9 HCHO	38.80	38.80	1.00	0.0093	0.0196
10 ALD2	20.00	40.00	2.00	0.0048	0.0101
12 RCHO	6.40	19.20	3.00	0.0015	0.0032
15 UR	2097.00	2184.00	1.04	0.5039	1.0604
Demerjian (1982)					
1 HC1	83.30	297.00	3.57	0.0200	0.0401
2 HC2	271.90	1239.50	4.56	0.0653	0.1310
3 HC3	65.20	98.00	1.50	0.0157	0.0314
4 HC4	58.30	441.00	7.56	0.0140	0.0281
5 UR	2048.00	2086.00	1.02	0.4921	0.9868
Killus and Whitten (1982)					
1 OLE	23.30	46.60	2.00	0.0056	0.0124
2 PAR	1334.10	1334.10	1.00	0.3206	0.7124
3 ARO	50.10	300.60	6.00	0.0120	0.0268
4 CARB	105.50	105.50	1.00	0.0254	0.0563
5 ETH	43.00	86.00	2.00	0.0103	0.0230
6 UR	2250.70	2288.70	1.00	0.5408	1.2018
McRae and Seinfeld (1983)					
1 HCHO	38.80	38.80	1.00	0.0093	0.0187
2 RCHO	26.40	59.20	2.24	0.0063	0.0127
3 ARO	58.30	441.00	7.56	0.0140	0.0281
4 C2H4	43.00	86.00	2.00	0.0103	0.0207
5 OLE	40.30	211.00	5.24	0.0097	0.0194
6 ALK	271.90	1239.50	4.56	0.0653	0.1310
7 UR	2048.00	2086.00	1.02	0.4921	0.9868

TABLE 42 (Continued)

CODE	ppbV	ppbC	C#	THC SPLIT ^a	RHC SPLIT ^b
Penner and Walton (1982)					
1 HC1	83.30	297.00	3.57	0.0200	0.0401
2 HC2	271.90	1239.50	4.56	0.0653	0.1310
3 HC3	58.30	441.00	7.56	0.0140	0.0281
4 HC4	65.20	98.00	1.50	0.0157	0.0314
5 UR ^c	2048.00	2086.00	1.02	0.4921	0.9868

Footnotes for Table 42

- (a) The THC split was obtained by dividing the ppbV concentration of each species by the ppbC THC concentration.
- i.e., The THC split for PRPA in the Atkinson et al. mechanism is $37.00/4161.5 = 0.0089$.
- (b) The RHC split was obtained by dividing the ppbV concentration of each species by the ppbC RHC concentration.
- i.e., The RHC split for PRPA in the Atkinson et al. mechanism is $37.00/1977.5 = 0.0187$.
- (c) In the Penner and Walton (1982) mechanism, these species are actually included in HC2 but their reactivity weights are extremely low and, hence, these species can be considered to be unreactive.

TABLE 43

Comparison of Splitting Factors for Different Reaction Mechanisms

MECHANISM	MEASUREMENTS ^a	APPROACH TO SPECIES ALLOCATION ^b																		
Atkinson et al. (1982)	----	No splitting factors have been developed because in all applications of this mechanism detailed measurements have been available to specify the initial conditions for each of the lumped classes.																		
Demerjian (1983)	NMHC	Splitting factors have been generated by Schere (1983) for apportioning non-methane hydrocarbon measurements made in St Louis. <table><tr><th>HC Class</th><th>St Louis</th><th>Profile Table 42</th></tr><tr><td>HC1</td><td>0.0657</td><td>0.0401 (0.61)</td></tr><tr><td>HC2</td><td>0.0786</td><td>0.1310 (1.67)</td></tr><tr><td>HC3</td><td>0.0810</td><td>0.0314 (0.39)</td></tr><tr><td>HC4</td><td>0.0248</td><td>0.0281 (1.13)</td></tr></table>	HC Class	St Louis	Profile Table 42	HC1	0.0657	0.0401 (0.61)	HC2	0.0786	0.1310 (1.67)	HC3	0.0810	0.0314 (0.39)	HC4	0.0248	0.0281 (1.13)			
HC Class	St Louis	Profile Table 42																		
HC1	0.0657	0.0401 (0.61)																		
HC2	0.0786	0.1310 (1.67)																		
HC3	0.0810	0.0314 (0.39)																		
HC4	0.0248	0.0281 (1.13)																		
Dodge (1977)	NMHC	There is no direct means for allocating hydrocarbon measurements to the surrogate species used in this mechanism. The default composition of the mixture used in EKMA is 25% propene and 75% n-butane (on a carbon basis). Formaldehyde and acetaldehyde are assumed to be present at 2% and 3% of the initial hydrocarbon level. <table><tr><th>HC Class</th><th>Default Split</th></tr><tr><td>PROP</td><td>0.0833</td></tr><tr><td>BUT</td><td>0.1875</td></tr><tr><td>HCHO</td><td>0.0200</td></tr><tr><td>ALD2</td><td>0.0150</td></tr></table>	HC Class	Default Split	PROP	0.0833	BUT	0.1875	HCHO	0.0200	ALD2	0.0150								
HC Class	Default Split																			
PROP	0.0833																			
BUT	0.1875																			
HCHO	0.0200																			
ALD2	0.0150																			
Killus & Whitten (1982a)	RHC	The default values used below are based on the recommendations given in Table 17 of Killus and Whitten (1982a) for typical urban hydrocarbon mixtures. <table><tr><th>HC Class</th><th>Recommended</th><th>Profile Table 42</th></tr><tr><td>OLE</td><td>0.0150</td><td>0.0124 (0.82)</td></tr><tr><td>PAR</td><td>0.6500</td><td>0.7124 (1.10)</td></tr><tr><td>ARO</td><td>0.0367</td><td>0.0268 (0.73)</td></tr><tr><td>CARB</td><td>0.0500</td><td>0.0563 (1.13)</td></tr><tr><td>ETH</td><td>0.0250</td><td>0.0230 (0.92)</td></tr></table>	HC Class	Recommended	Profile Table 42	OLE	0.0150	0.0124 (0.82)	PAR	0.6500	0.7124 (1.10)	ARO	0.0367	0.0268 (0.73)	CARB	0.0500	0.0563 (1.13)	ETH	0.0250	0.0230 (0.92)
HC Class	Recommended	Profile Table 42																		
OLE	0.0150	0.0124 (0.82)																		
PAR	0.6500	0.7124 (1.10)																		
ARO	0.0367	0.0268 (0.73)																		
CARB	0.0500	0.0563 (1.13)																		
ETH	0.0250	0.0230 (0.92)																		

TABLE 43 (Continued)

MECHANISM	MEASUREMENTS ^a	APPROACH TO SPECIES ALLOCATION ^b		
McRae and Seinfeld (1983) THC	These splitting factors have been developed to partition total hydrocarbon measurements for conditions occurring during 1974 in Los Angeles. The coefficients were compiled from McRae and Seinfeld (1983)			
	HC Class	Los Angeles	Profile Table 42	
	HCHO	0.0118	0.0093	(0.79)
	RCHO	0.0043	0.0063	(1.46)
	ARO	0.0075	0.0140	(1.87)
	C2H4	0.0247	0.0103	(0.42)
	OLE	0.0110	0.0097	(0.88)
	ALK	0.0419	0.0653	(1.56)
Penner and Walton (1983) NMHC	The default values used for splitting ambient measurements of non-methane hydrocarbons for San Francisco are based on Penner (1982). ^(c)			
	HC Class	San Francisco	Profile Table 42	
	HC1	0.025	0.0401	(1.60)
	HC2	0.1625	0.1310	(0.81)
	HC3	0.050	0.0281	(0.56)
	HC4	0.0075	0.0314	(4.19)

Footnotes for Table 43

(a) The codes used to identify measurements expressed on a carbon basis are:

NMHC - Non-methane hydrocarbons
 RHC - Reactive hydrocarbons
 THC - Total hydrocarbons

Note that the U.S. Environmental Protection Agency has an additional class defined as Non-reactive Organic Gases (NROG) that contains those species not considered to be ozone precursors. The compounds are: methane, ethane, methylene chloride, methyl chloroform, trifluoromethane, trichlorotrifluoroethane, trichlorofluoromethane, chlorodifluoromethane, dichlorodifluoromethane, dichlorotetrafluoroethane and chloropentafluoroethane. Further details are contained in 42 FR 48941 - July 8.

(b) The numbers in brackets () are the ratio of the splitting factors derived from Table 42 and the procedures recommended for partitioning ambient measurements.

(c) Shown for comparison only. In actual implementation, reactivity weighting factors are used.

involve carbonyl compounds. There is a great need for additional field measurements of these compounds.

The carbon bond concentrations for ETH, OLE, ARO and CARB are exactly comparable to molecular concentrations in the atmosphere. To compare PAR requires an extremely detailed knowledge of all species, but PAR can be used along with the carbon numbers of the carbon bond species to compare the THC or RHC values in ppmC units. For example, the THC splits for the Atkinson et al. (1982) mechanism can be compared with the carbon bond splits using Table 42 as follows:

THC Splits			
<u>Carbon Bond Species</u>	<u>KW</u>	<u>ALW</u>	<u>ALW Species</u>
ETH	0.0103	0.0103	ETHE
ARO	0.0120	0.0120	TOLU + XYEN
OLE	0.0056	0.0058	PRPE
CARB	0.0254	0.0234	HCHO + ALD2 + RCHO + 2x BUTE

The minor differences in OLE and CARB occur because 2,2-dimethyl-1-butene and the cycloparaffins reactivities were interpreted differently. Whitten (private communication, 1983) has analyzed some of the original data from which Calvert (1976) generated the data presented in Table 41 and has found that 2,2-dimethyl-1-butene should be 2,3-dimethyl-1-butene and that compound 18 of Table 41 should probably be cyclohexane rather than cyclohexene.

Another approach to the development of splitting factors for ambient air quality data is to assume that ambient hydrocarbon compositions are similar to emissions. Bucon et al. (1978) and Trijonis and

Arledge (1975) have compiled detailed composition profiles for many of the source classes that are likely to be encountered in atmospheric modeling applications. Given estimates of reactive hydrocarbon emissions from each source class these profiles can be used to develop a chemically resolved inventory. In much the same manner as above, the detailed emissions inventory can be used to develop splitting factors. Usually these factors should only be applied to reactive hydrocarbon measurements because of the uncertainties associated with estimating total emissions in an urban airshed (McRae and Seinfeld, 1983). A typical example of the application of this technique is presented in Table 44. There is almost a factor of three difference between the carbonyl splitting factors based on air quality data and those derived from the emissions inventory. Without further emissions and air quality data it will be difficult to account accurately for these discrepancies.

In summary, if chemically resolved modeling approaches are to be used in urban environments both the emissions inventory data and the ambient hydrocarbon measurements need to be improved to the point where they have the same chemical resolution as the requirements of the particular photochemical mechanism. Unless this is carried out, the large uncertainties in specifying initial conditions may negate any improvements in air quality predictions that may arise as a result of the use of more sophisticated chemical mechanisms.

5.4 Conclusions

In this chapter the primary goal has been to present a comparison of the way in which the initial conditions and rate constants for

TABLE 44

Hydrocarbon Splitting Factors for McRae and Seinfeld (1983) Mechanism
Based on Los Angeles Emissions Inventory for 1974^a

SPECIES ^b	KG/SEC	MW	MOLES/SEC	C#	MOLES/SEC OF CARBON	CARBON FRACTION	RHC SPLIT
HCHO	0.18	30.0	6.00	1.00	6.00	0.0060	0.0060
RCHO	0.25	63.1	3.96	3.36	13.30	0.0133	0.0040
ARO	2.03	100.2	20.26	7.56	153.17	0.1528	0.0202
C2H4	0.82	28.0	29.29	2.00	58.58	0.0584	0.0292
OLE	1.98	67.4	29.38	4.83	141.25	0.1409	0.0292
ALK	9.04	83.5	108.26	5.82	630.07	0.6286	0.1080
Totals	14.30		197.15		1002.37		

Footnotes for Table 44

(a) The emissions inventory is based on McRae and Seinfeld (1983).

(b) Emissions of terpenes have not been included.

lumped hydrocarbon steps are treated in each of the reaction mechanisms. If a detailed hydrocarbon profile is available, the procedures to be followed for specifying the initial conditions and rate constants for the lumped classes are relatively straightforward. On the other hand, if the only measurements are total or reactive hydrocarbons the problem of establishing the initial conditions is considerably more difficult and leads to substantial uncertainties. The use of organic lumping schemes imposes a requirement that both the organic emission inventory and ambient monitoring data have the same resolution as the chemical mechanism. There is a critical need for comprehensive studies of both the composition and amount of organics emitted into urban environments. Particular attention needs to be given to carbonyl compounds. Without this information the uncertainties in specifying the input data can overwhelm the improvements in air quality predictions that might arise from the use of a more refined mechanism.

CHAPTER 6

CONCLUSIONS

This report has presented a detailed description of six lumped reaction mechanisms for photochemical smog:

Atkinson et al. (1982)

Demerjian (1982)

Dodge (1977)

Killus and Whitten (1982a)

McRae and Seinfeld (1983)

Penner and Walton (1982)

The description includes a discussion of the basic assumptions in each mechanism's treatment of the fundamental chemistry, photolysis reactions, and organic lumping via initial conditions and organic rate constants. In general, it is found that the mechanisms differ in virtually all aspects, and, without detailed, quantitative, numerical comparisons, it is difficult to predict simply from inspection how each mechanism will perform in a particular application. Nevertheless, if one removes those mechanism aspects included only to account for smog chamber-dependent radical sources, such as a wall source of OH radicals or initial HONO, it is possible to rank the mechanisms according to overall "reactivity." We find on the basis of our analysis that such a ranking is:

Killus and Whitten (1982a)	}	most reactive
Demerjian (1982)		
McRae and Seinfeld (1983)		

Atkinson et al. (1982)	}	less reactive
Penner and Walton (1982)		

The Dodge (1977) mechanism cannot be ranked in this scale because the split between propene and n-butane is fixed.

Our object is to be able to tell specifically what aspects of each mechanism are key to its performance, as measured by its "reactivity." To do so requires the detailed, quantitative, numerical comparisons referred to above. Such comparisons are the subject of Part II.

REFERENCES

- Altshuller, A.P. and Bellar, T.A. (1963), "Gas Chromatographic Analysis of Hydrocarbons in the Los Angeles Atmosphere," J. Air Pollution Control Association, 13, 81-87.
- Altshuller, A.P., Lonneman, W.A., Sutterfield, F.D. and Kopczynski, S.L. (1971), "Hydrocarbon Composition of the Atmosphere of the Los Angeles Basin," Environmental Science and Technology, 5, 1009-1016.
- Atkinson, R. and Lloyd, A.C. (1983), "Evaluation of Kinetic and Mechanistic Data for Modeling of Photochemical Smog," J. Phys. Chem. Ref. Data (in press).
- Atkinson, R., Darnall, K.R., Lloyd, A.C., Winer, A.M. and Pitts, J.N. Jr. (1979), "Kinetics and Mechanisms of the Reaction of the Hydroxyl Radical with Organic Compounds in the Gas Phase," Advances in Photochemistry, 11, 375-488.
- Atkinson, R., Lloyd, A.C. and Wines, L. (1982), "An Updated Chemical Mechanism for Hydrocarbons/NO_x/SO₂ Photooxidations Suitable for Inclusion in Atmospheric Simulation Models," Atmospheric Environment, 16, 1341-1355.
- Bass, A.M., Glasgow, L.C., Miller, C., Jesson, J.P. and Filkin, D.L. (1980), "Temperature Dependent Absorption Cross Sections for Formaldehyde (CH₂O): The Effect of Formaldehyde on Stratospheric Chlorine Chemistry," Planetary and Space Science, 28, 675-679.
- Baulch, D.L., Cox, R.A., Hampson, R.F., Kerr, J.A., Troe, J. and Watson, R.T. (1980), "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry," J. Physical and Chemical Reference Data, 9, 295-471.
- Baulch, D.L., Cox, R.A., Crutzen, P.J., Hampson, R.F., Kerr, J.A., Troe, J. and Watson, R.T. (1982), "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry: Supplement 1. CODATA Task Group on Chemical Kinetics," J. Physical and Chemical Reference Data, 11, 327-496.
- Braslau, N. and Dave, J.V. (1973a), "Effect of Aerosols on the Transfer of Solar Energy through Realistic Model Atmospheres, Part I: Non-Absorbing Aerosols," J. Applied Meteorology, 12, 601-615.
- Braslau, N. and Dave, J.V. (1973b), "Effect of Aerosols on the Transfer of Solar Energy through Model Atmospheres, Part II: Partly - Absorbing Aerosols," J. Applied Meteorology, 12, 616-619.

- Bucon, H.W., Malko, J.F. and Taback, H.J. (1978), Volatile Organic Compound (VOC) Species Data Manual, U.S. Environmental Protection Agency Report No. EPA-450/3-78-119.
- Calvert, J.G. (1976), "Hydrocarbon Involvement in Photochemical Smog Formation in Los Angeles Atmosphere," Environmental Science and Technology, 10 256-262.
- Carter, W.P.L., Lloyd, A.C., Sprung, J.L. and Pitts, J.N. Jr. (1979) "Computer Modeling of Smog Chamber Data: Progress in Validation of a Detailed Mechanism for the Photooxidation of Propane and n-Butane in Photochemical Smog," Int. J. Chemical Kinetics, XI, 45-101.
- Carter, W.P.L., Winer, A.M. and Pitts, J.N., Jr. (1982) "Effect of Kinetic Mechanisms and Hydrocarbon Composition on Oxidant-Precursor Relationships Predicted by the EKMA Isopleth Technique," Atmospheric Environment, 16, 113-120.
- Darnall, K.R., Atkinson, R. and Pitts, J.N. (1979), "Observation of Biacetyl from the Reaction of OH Radicals with o-Xylene: Evidence for Ring Cleavage," J. Physical Chemistry, 83, 1943-1946.
- Demerjian, K.L., Schere, K.L. and Peterson, J.T. (1980), "Theoretical Estimates of Actinic (Spherically Integrated) Flux and Photolytic Rate Constants of Atmospheric Species in the Lower Troposphere," Advances in Environmental Science and Technology, 10, 369-459.
- Demerjian, K.L. (1982), "Personal Communication."
- DeMore, W.B., Watson, R.T., Howard, C.J., Golden, D.M., Molina, M.J., Hampson, R.F., Kurylo, M. and Ravishankara, A.R. (1982), Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Jet Propulsion Laboratory Publication 82-57, California Institute of Technology, Pasadena, California.
- Dodge, M.C. (1977), "Combined Use of Modeling Techniques and Smog Chamber Data to Derive Ozone--Precursor Relationships," U.S. Environmental Protection Agency Report, EPA-600/3-77-001a, 881-889.
- Durbin, P.A., Hecht, T.A. and Whitten, G.Z. (1975), "Mathematical Modeling of Simulated Photochemical Smog," U.S. Environmental Protection Agency Report, EPA-650/4-75-026.

- Edelson, D. (1975), "The New Look in Chemical Kinetics," J. Chemical Education, 52, 642-644.
- Edelson, D. (1976), "A Simulation Language and Compiler to Aid Computer Solution of Chemical Kinetic Problems," Computers and Chemistry, 1, 29-33.
- Edelson, D. (1981), "Computer Simulation in Chemical Kinetics," Science, 214, 981-986.
- Falls, A.H. and Seinfeld, J.H. (1978), "Continued Development of a Kinetic Mechanism for Photochemical Smog," Environmental Science and Technology, 12, 1398-1406.
- Falls, A.H., McRae, G.J. and Seinfeld, J.H. (1979), "Sensitivity and Uncertainty of Reaction Mechanisms for Photochemical Air Pollution," Int. J. Chemical Kinetics, 11, 1137-1162.
- Gelinas, R.J., Dickerson, R.P. and Grant, K.E. (1974), Solar Flux and Photodissociation Calculations for LLL Atmospheric Physics Programs, Lawrence Livermore Laboratory Report UCRL-74944 Rev. 1, Lawrence Livermore National Laboratory, University of California, Livermore, California.
- Gelinas, R.J. and Skewes-Cox, P.D. (1977), "Tropospheric-Photochemical Mechanisms," J. Physical Chemistry, 81, 2468-2479.
- Gradel, T.E. (1978), Chemical Compounds in the Atmosphere, Academic Press, New York.
- Greiner, N.R. (1970), "Hydroxyl Radical Kinetics by Kinetic Spectroscopy VI. Reactions with Alkanes in the Range 300-500 °K," J. Chemical Physics, 53, 1070-1076.
- Hampson, R.F. and Garvin, D. (1978), "Reaction Rate and Photochemical Data for Atmospheric Chemistry - 1977," U.S. Department of Commerce National Bureau of Standards Special Publication 513, 111 pp.
- Hindmarsh, A.C. (1980), "LSODE and LSODI, Two New Initial Value Ordinary Differential Equation Solvers," ACM-Signum Newsletter, 15, 10-11.
- Horowitz, A. and Calvert, J.G. (1982), "Wavelength Dependence of the Primary Processes in Acetaldehyde Photolysis," J. Physical Chemistry, 86, 3105-3114.
- Hudson, R.D. and Reed, E.I. eds. (1979), The Stratosphere: Present and Future, NASA Reference Publication No. 1049.

- Jeffries, H.E., Sexton, K.G. and Salmi, C.N. (1981), Effects of Chemistry and Meteorology on Ozone Control Calculations Using Simple Trajectory Models and the EKMA Procedure, Final Report to the U.S. Environmental Protection Agency Under Contract No.68-02-3523, School of Public Health, University of North Carolina, Chapel Hill, North Carolina, 373 pp.
- Jettes, R. and Burghardt, E. (1972), "Automatic Gas Chromatographic Measurement of C₁-C₅ Hydrocarbons in Air," Atmospheric Environment, 6, 793-805.
- Kee, R.J., Miller, J.A. and Jefferson, T.H. (1980), CHEMKIN: A General Purpose, Problem-Independent, Transportable, FORTRAN Chemical Kinetics Code Package, Sandia Laboratories Report No. SAND80-8003, Albuquerque, New Mexico, 204 pp.
- Killus, J.P. (1982a), "Personal Communication - 26 August 1982"
- Killus, J.P. (1982b), "Computer Output - 23 August 1982"
- Killus, J.P. and Whitten, G.Z. (1982a), A New Carbon-Bond Mechanism for Air Quality Modeling, U.S. Environmental Protection Agency Report No. EPA-600/3-82-041.
- Killus, J.P. and Whitten, G.Z. (1982b), "A Mechanism Describing the Photochemical Oxidation of Toluene in Smog," Atmospheric Environment, 16, 1973-1988.
- Kopczynski, S.L., Kuntz, R.L. and Bufalini, J.J. (1975), "Reactivities of Complex Hydrocarbon Mixtures," Environmental Science and Technology, 9, 648-653.
- Kopczynski, S.L., Lonneman, W.A., Sutterfield, F.D. and Darley, P.E. (1972), "Photochemistry of Atmospheric Samples in Los Angeles," Environmental Science and Technology, 6, 342-347.
- Kramer, M.A., Kee, R.J. and Rabitz, H. (1982), CHEMSEN: A Computer Code for Sensitivity Analysis of Elementary Chemical Reaction Models, Sandia Laboratories Report No. SAND82-8230, Albuquerque, New Mexico, 23 pp.
- Kramer, M.A., Calo, J.M. and Rabitz, H. (1981), "An Improved Computational Method for Sensitivity Analysis: Green's Function Method with 'AIM'," Applied Mathematical Modelling, 5, 432-441.
- Koda, M., McRae, G.J. and Seinfeld, J.H. (1979), "Automatic Sensitivity Analysis of Reaction Mechanisms," Int. J. Chemical Kinetics, 11, 427-444.

- Lamb, S.I., Petrowski, C., Kaplan, I.R. and Simoneit, B.R.T. (1980), "Organic Compounds in Urban Atmospheres: A Review of Distribution Collection and Analysis," J. Air Pollution Control Association, 30, 1098-1115.
- Leighton, P.A. (1961), Photochemistry of Air Pollution, Academic Press, New York, 300 pp.
- Leinster, P., Perry, R. and Young, R.J. (1977), "Detection and Measurement of Volatile Hydrocarbons at Ambient Concentrations in the Atmosphere," Talanta, 24, 205-213.
- Leone, J.A. and Seinfeld, J.H. (1983) "Analysis of the Characteristics of Complex Chemical Reaction Mechanisms - Application to Photochemical Smog Chemistry," (submitted for publication).
- Lonneman, W.A., Seila, R.L. and Bufalini, J.J. (1978), "Ambient Air Hydrocarbon Concentrations in Florida," Environmental Science and Technology, 12, 459-463.
- Lonneman, W.A., Kopczynski, S.L., Darley, P.E. and Sutterfield, F. (1974), "Hydrocarbon composition of Urban Air Pollution," Environmental Science and Technology, 8, 229-236.
- Lurmann, F. (1982), "Personal Communication - Computer Listing."
- Lurmann, F. (1983), "Personal Communication - HC Speciation."
- Luther, F.M. and Gelinas, R.J. (1976), "Effects of Molecular Multiple Scattering and Surface Albedo on Atmospheric Photodissociation Rates," J. Geophysical Research, 81, 1125-1132.
- MacCracken, M.C. and Sauter, G.C. eds. (1975), "Development of an Air Pollution Model for the San Francisco Bay Area," Final Report to the National Science Foundation, Lawrence Livermore Report UCRL-51920, 1169 pp.
- Magnotta, F. and Johnston, H.S. (1980), "Photodissociation Quantum Yields for the NO_3 Free Radical," Geophysical Research Letters, 7, 769-772.
- McRae, G.J. (1983), Computer Programs for the Solution and Analysis of Chemical Systems: User Manual, Environmental Quality Laboratory, California Institute of Technology, Pasadena, California. (In preparation).
- McRae, G.J., Goodin, W.R. and Seinfeld, J.H. (1982), "Development of a Second-Generation Mathematical Model for Urban Air Pollution I. Model Formulation," Atmospheric Environment, 16, 679-696.

- McRae, G.J. and Seinfeld, J.H. (1983), "Development of a Second-Generation Mathematical Model for Urban Pollution II: Model Performance Evaluation," Atmospheric Environment, 17, 501-523.
- McRae, G.J., Tilden, J.W. and Seinfeld, J.H. (1982), "Global Sensitivity Analysis - A Computational Implementation of the Fourier Amplitude Sensitivity Test (FAST)," Computers and Chemical Engineering, 6, 15-25.
- Molina, L.T., Schinke, S.D. and Molina, M.J. (1977), "Ultraviolet Absorption Spectrum of Hydrogen Peroxide Vapor," Geophysics Research Letters, 4, 580-582.
- Moortgat, G.K., Klippel, W., Mobius, K.H., Seiler, W., and Warneck, P. (1980) Laboratory Measurements of Photolytic Parameters for Formaldehyde, Federal Aviation Administration Report No. FAA-EE-80-47, U.S. Department of Transportation, Office of Environment and Energy, Washington, D.C.
- Neligan, R.E. (1962), "Hydrocarbons in the Los Angeles Atmosphere," Archives of Environmental Health, 5, 581-591.
- Niki, H., Maker, P.D., Savage, C.M. and Breitenbach, L.P. (1977) "Fourier Transform IR Spectroscopic Observation of Propylene Ozonide in the Gas-Phase Reaction of Ozone-Cis-2-Butene-Formaldehyde," Chem. Phys. Letters, 46, 327-330.
- Penner, J.E. and Walton, J.J. (1982) Air Quality Model Update, Lawrence Livermore Laboratory Report UCID - 19300, Lawrence Livermore National Laboratory, University of California, Livermore, California, 55 pp.
- Peterson, J.T. (1976), "Calculated Actinic Fluxes (290-700 nm) for Air Pollution Photochemistry Application," U.S. Environmental Protection Agency Report EPA-600/4-76-025, 63 pp.
- Peterson, J.T., Demerjian, K.L. and Schere, K.L. (1977), "Actinic Solar Flux and Photolytic Rate Constants in the Troposphere," Proc. International Conference on Photochemical Oxidant and its Control, Vol II, Raleigh, North Carolina, Sept. 12-17, 1976, NTIS PB-264 233, 763-773.
- Pitts, J.N., Winer, A.M., Darnall, K.R. et al. (1976), Chemical Consequences of Air Quality Standards and of Control Implementation Programs: Roles of Hydrocarbons, Oxides of Nitrogen, and Aged Smog in the Production of Photochemical Oxidant, Final Report to the California Air Resources Board under Contract Number 4-212, Statewide Air Pollution Research Center, University of California Riverside, California, 444 pp.

- Plum, C.N., Sanhueza, E., Atkinson, R., Carter, W.P.L. and Pitts, J.N. (1983), "OH Radical Rate Constants and Photolysis Rates of Alpha-Dicarbonyls," Environmental Science and Technology, (In Press).
- Schere, K.L. (1983), "Personal Communication - Letter dated 14 January."
- Schere, K.L. and Demerjian, K.L. (1977), "Calculation of Selected Photolytic Rate Constants Over A Diurnal Range," U.S. Environmental Protection Agency, Report EPA-600/4-77-015, 71 pp.
- Simoneit, B.R.T. and Mazurek, M.A. (1981), "Air Pollution: The Organic Components," CRC Critical Reviews in Environmental Control, 11(3), 219-276.
- Stedman, D.H., Harvey, R.B. and Dickerson, R.R. (1977), "Measurement of Photons Indicated in Photochemical Oxidant Formation," Proc. International Conference on Photochemical Oxidant and its Control, Vol II, Raleigh, North Carolina, NTIS PB-264 233, 753-762.
- Stephens, E.R. and Hellrich, O.P. (1980), "Chromatographic Monitoring of Hydrocarbons in Ambient Air," Environmental Science and Technology, 14, 836-838.
- Stephens, E.R. and Burleson, F.R. (1969), "Distribution of Light Hydrocarbons in Ambient Air," J. Air Pollution Control Association, 19, 929-936.
- Trijonis, J.C. and Arledge, K.W. (1975), Utility of Reactivity Criteria in Organic Emissions Control Strategies for Los Angeles, TRW Corporation, Final report to the U.S. Environmental Protection Agency under Contract No. 68-02-1735, Los Angeles, California.
- Whitten, G.Z., and Hogo, H. (1978), User's Manual for Kinetics Model and Ozone Isopleth Plotting Package, U.S. Environmental Protection Agency Report No. EPA-600/8-78-014a, Prepared by Systems Application Inc., San Rafael, California, 35 pp.
- Whitten, G.Z., and Hogo, H. (1980), Modeling of Simulated Photochemical Smog with Kinetic Mechanisms: Volume 2 CHEMK - A Computer Modeling Scheme for Chemical Kinetics, U.S. Environmental Protection Agency Report No. EPA-600/3-80-028b, Prepared by Systems Application Inc., San Rafael, California, 113 pp.
- Whitten, G.Z., Hogo, H. and Killus, J.P. (1980a), "The Carbon-Bond Mechanism: A Condensed Kinetic Mechanism for Photochemical Smog," Environmental Science and Technology, 14, 690-700.

Whitten, G.Z., Hogo, H. and Killus, J.P. (1980b), Modeling of Simulated Photochemical Smog with Kinetic Mechanisms: Volume 1, U.S. Environmental Protection Agency Report No. EPA-600/3-80-028a, Prepared by Systems Applications Inc., San Rafael, California, 362 pp.

Whitten, G.Z. (1981) Comments at U.S. Environmental Protection Agency Workshop on the Empirical Kinetic Modeling Approach, December 15-16, Research Triangle Park, NC.

Winer, A.M., Brauer, G.M., Carter, W.P.L., Darnall, K.R. and Pitts, J.N., Jr. (1979) "Effects of Ultraviolet Spectral Distribution on the Photochemistry of Simulated Polluted Atmospheres," Atmospheric Environment, 13, 989-998.

WMO (1981), The Stratosphere 1981 Theory and Field Measurements, World Meteorological Organization Global Ozone Research and Monitoring Project Report No. 11, World Meteorological Organization, Geneva, Switzerland.

Zafonte, L., Rieger, P.L. and Holmes, J.R., (1977), "Nitrogen Dioxide Photolysis in the Los Angeles Atmosphere," Environmental Science and Technology, 11, 483-487.